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FIRE HAZARDS IN THE USE OF OXIDIZING AGENTS AS HERBICIDES[1]

BY W. H. COOK[2]

Abstract

The combustibility of organic matter-sodium chlorate mixtures in various proportions has been tested at different relative humidities. It was found that mixtures containing more than 10% of sodium chlorate are sufficiently combustible to be hazardous at all relative humidities below 75% but are non-hazardous at higher humidities. Data were obtained showing the minimum moisture content required for protecting such mixtures and this information may be used to calculate the approximate amount of any water-absorbing chemical that has to be added to sodium chlorate to render it safe. Admixture of calcium chloride or magnesium chloride with the sodium chlorate renders the mixture safe when these protecting salts form one-half and one-third respectively of the resulting herbicide. Judging from the chlorate content the above sodium chlorate-magnesium chloride mixture would be the most effective "safe" herbicide of those tested, but it would be about only half as toxic as pure sodium chlorate. Several other salts were tested as protecting agents but they were either ineffective or resulted in the decomposition of the chlorate. Combustibility tests were also conducted on barium chlorate- and calcium chlorate-organic matter mixtures. These mixtures are less inflammable than those containing sodium chlorate but are sufficiently combustible to be a fire hazard in districts where the atmospheric humidity is low. Addition of one part of anhydrous calcium chloride or magnesium chloride to two parts of barium chlorate results in a safe mixture. Sodium dichromate-organic matter mixtures are much less combustible than those containing chlorate, but these mixtures also are somewhat dangerous at ordinary humidities when there is a high proportion of sodium dichromate in the mixture. When 10% of anhydrous calcium or magnesium chloride is added to the sodium dichromate the resultant mixture is safe under ordinary atmospheric humidities, regardless of the proportion of organic matter present. Mixtures of sodium chlorate and sodium dichromate with organic material are extremely combustible.

Introduction

The fire hazards associated with the use of strong oxidizing agents as herbicides have been made the subject of this investigation. Sodium chlorate is an example of the class of chemical concerned and is the one most commonly used for killing perennial weeds. This compound is relatively safe to

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handle in the pure form but under farm conditions it commonly becomes mixed with organic material, and the resulting mixture is readily ignited by a spark, heat or friction. Solutions of sodium chlorate can be handled quite safely, but unfortunately they dry rapidly and completely, leaving contaminated wooden vessels, clothes, or plant material an extreme fire hazard. A possible method of reducing this risk is to mix sodium chlorate with chemicals of high water-absorbing capacity, or with other non-oxidizing chemicals of good herbicidal power, the latter acting as a diluent and a fire preventive when in contact with organic material. Such mixtures have been investigated, particularly in regard to the relative humidity and the proportions of the various chemicals necessary to reduce the danger of fire. The alternative possibility of supplying the chlorate ion in another combination, such as calcium chlorate and barium chlorate has also been studied from the standpoint of fire risk.

Sodium dichromate is also used to some extent as a herbicide. Preliminary work (2) indicates that this compound is quite toxic to annual weeds, but its value for killing perennials is still doubtful.

Review

Sodium and potassium chlorate form a major part of the so-called "chloratites" and "cheddites" which are explosives of the "blasting" type. A typical cheddite contains 70 to 90% potassium chlorate mixed with an aromatic nitro compound and paraffin. The data given in the International Critical Tables (9) show that these explosives are more sensitive to shock, judging from the fall-hammer test, and have a higher heat of explosion, than black powder. The shock sensitivity and heat of explosion will naturally depend on the amount, kind, and physical state of the combustible material, but the above comparison gives some idea of the kind of explosive resulting when sodium chlorate is mixed with organic material.

The fire risk involved in the use of sodium chlorate has been recognized by those who have recommended its use as a herbicide. Nearly every circular and bulletin dealing with the herbicidal qualities of sodium chlorate includes warnings about its dangerous character when mixed with organic material. An editorial in Industrial and Engineering Chemistry (5) issues a warning about the use of sodium chlorate as a farm herbicide. This article states that sodium chlorate packed in metal containers is safe as long as it remains in the closed container, and of itself is not dangerous, inflammable, nor explosive. It is pointed out however that this safe chemical becomes an extremely dangerous one when the container is opened on the farm where admixture with organic dusts will result unless every precaution is taken.

In spite of the above warnings some bad burning accidents have occurred from the use of sodium chlorate. The writer of the above editorial claims to have been informed that fields sprayed with chlorate have ignited spontaneously on hot days; that vehicles used for carrying spray solution have later taken fire, probably owing to a jar or the heat of the sun; and that buildings

have been destroyed by fire apparently as the result of the solution drying or of dust settling on the chlorate. Deem (3) reports that a man's clothing, which had become wetted with chlorate solution, caught fire several days afterwards, in spite of the fact that he had soaked the clothing overnight in a tin of water after the spraying operation. The writer knows of two instances in which clothing, soaked with chlorate, has been accidentally ignited by friction after drying.

It is difficult for the non-technical man to realize the extremely dangerous character of sodium chlorate. Knowing nothing about the nature of the compound, he does not realize that although the pure chemical and its solutions are non-combustible, a mixture of it with organic matter yields material even more dangerous than gasoline, since it can be ignited by friction and shock as well as by a spark. Moreover, even if sodium chlorate is handled cautiously, it is almost certain that some of the chemical will come in contact with wagons and other farm equipment, unless special machinery is used for handling it, an arrangement which is impracticable on the ordinary farm. Indeed the sprayed plants themselves constitute fire hazards. To overcome this risk Loomis, Bissey, and Smith (7) have recommended that the top growth of the plants be removed before treating, and the chlorate salt applied to the soil. They claim that this method is as effective as the application of the spray to the growing plants.

Considering all factors it would seem best, in the interests of safety, to mix the chlorates with other chemicals which would reduce the fire hazard to a minimum, and if possible to have the resulting mixture possess, as nearly as possible, the same herbicidal power as the original material.

The possibility of reducing the fire hazard by the addition of other chemicals has been recognized by the manufacturers of commercial chlorate herbicides. Analyses of several chlorate weed killers show that approximately 60% of the dry solid is sodium chlorate and 40% is calcium chloride. Calcium chloride is much less toxic to plants than sodium chlorate and may be regarded as practically inert material. The chief function of the calcium salt is to reduce the fire hazard by absorbing moisture, although it is also claimed to improve the herbicide by preventing the chlorate from drying on the leaves and then blowing off. Arny, Bridgford, and Dunham (1) state that the presence of calcium chloride in Atlacide, a commercial herbicide, reduces the fire hazard, but does not remove it entirely.

Other commercial weed killers contain on a dry basis from 50 to 90% of sodium chlorate and from 10 to 50% of sodium carbonate. The reason for the admixture of the carbonates is not stated by the manufacturers, but it could scarcely be expected to reduce the fire risk, at ordinary atmospheric humidities, by the retention of moisture. At the temperature of combustion the decomposition of the carbonate with the evolution of carbon dioxide might retard the spreading of flame. Sodium carbonate might also reduce the fire risk by acting as a diluent, but this would also tend to reduce the herbicidal power of the mixture proportionally, since sodium carbonate alone

is less toxic to plants than the chlorates (2). It is possible, on the other hand, that the alkaline reaction which the carbonate would impart to the solution might increase the herbicidal power of the chlorate somewhat, but as yet there is little reliable information on this point.

Brief mention should be made of the explosive properties attributed by some writers to pure sodium chlorate, for even in the absence of organic matter this compound may break down into sodium chloride and free oxygen. Opinion seems to differ on this point, some authors (1, 5) believing that the pure chemical is quite safe while others (8, 12) consider it dangerous. Probably none of these investigators have studied the reaction critically. Lewis and Randall (6) from a consideration of the free energy and heat of formation of potassium chlorate, state that this chemical by itself is unstable, but would hardly be violently explosive. Since this statement will also apply to sodium chlorate, there seems to be little danger of this compound exploding. Mixing chlorates with water-absorbing chemicals in order to reduce the fire hazard when it is in contact with organic material would doubtless render the pure sodium chlorate entirely safe.

Experimental Material

The organic materials with which chlorates may come in contact will vary considerably in their inflammability. It was therefore necessary to select a readily combustible material for test purposes, in order that the protective action of any particular chemical or treatment might apply generally. Whatman No. 50 hardened filter paper was chosen first since it is essentially pure cellulose and therefore more completely combustible than the organic materials which will usually be met with in practice. Even this hardened paper, however, disintegrated somewhat on being soaked in the various solutions, and although it was used in certain experiments, it was found that cloth was more convenient to handle and yielded more accurate data. The cloth used was a 12-oz. duck. This material was thoroughly washed and rinsed with distilled water before use. It contained about 0.5% ash on an oven-dry basis.

Experimental Method

The method employed consisted essentially of treating the organic material, either cloth or filter paper, by soaking it in a solution of the oxidizing agent under test, then conditioning the treated material at a known relative humidity, and finally testing the inflammability of the treated and conditioned material.

Before starting a series of tests the cloth to be used was cut into two-inch squares, weighing about 1¼ gm. each. These pieces were numbered and a piece of cotton thread attached to each for hanging in the conditioning chamber. When filter paper was used three pieces 7 cm. in diameter had to be fastened together to get about the same weight of material. A piece of copper wire of known weight was used to fasten the pieces together and to provide a hanger.

The first step was to obtain the dry weight of the test material. A large number of pieces were placed in the conditioning chamber over sulphuric acid, and allowed to remain until their weights reached equilibrium. A few of these pieces were then placed over phosphorus pentoxide *in vacuo* at room temperature and if a further loss in weight took place the weights of the pieces in the conditioner were calculated to a bone-dry basis. This drying procedure was adopted since it was also suitable for treated material that could not be oven-dried.

The test pieces were treated by soaking them in solutions of the oxidizing agents to be tested. The solution under test was placed in a vapor-tight vessel and the pieces submerged for one hour. The material was then raised up out of the solution and allowed to drain at the vapor pressure of the solution for two hours in the same tight vessel. After draining, the pieces were allowed to dry in the room before placing them over sulphuric acid in the conditioning chamber. When the test pieces had reached equilibrium over the sulphuric acid, a few pieces were dried over phosphorus pentoxide as previously described for the untreated material. The amount of oxidizing agent, taken up from the solution, could then be calculated from the dry weights of the untreated and treated material.

By treating the test material with solutions of the oxidizing agent, as described above, a uniform treatment of all material was ensured. Furthermore the percentage of oxidizing agent in the treated material could easily be varied by using solutions of different concentrations, and any proportion or concentration of other salts, to be tested for protective action, could be easily obtained by varying the composition of the solution.

In order to determine the combustibility of the treated material under different atmospheric conditions it was necessary to conduct tests over a wide range of relative humidities. It was also important to determine the minimum moisture content required to give protection to the treated material, for these results could be used to estimate the amount of any water-absorbing chemical that would have to be added to the oxidizing agent to remove the fire risk. For these determinations it was necessary to construct a conditioning cabinet capable of maintaining the required relative humidities, and fitted with a balance so that the individual pieces could be weighed.

A drawing of the conditioning chamber is shown in Fig. 1. It consists of a closed chamber having a removable lid which fits into an oil seal. A window and small door were provided in the front of the chamber. This door, which was used for removing the individual pieces for test, consisted of an outer metal door, and an inner one constructed from four overlapping pieces of dental rubber dam stretched over a metal frame. By removing the outer door it was possible for the operator to put his hand into the chamber and take out the test pieces with the minimum exchange of air since the rubber passed quite snugly over the contour of the hand and wrist. The window and outer door were sealed in with plasticine. The chamber was provided with a De Khotinsky thermoregulator, two carbon filament lamps for heating, a

copper water-cooling coil, an air circulating fan, a turntable for holding the test pieces, and a rack for three glass trays. The temperature was kept at 25° C. ± 0.1° C. throughout these experiments. The relative humidity was controlled by placing concentrated sulphuric acid or a series of saturated salt solutions having known vapor pressures (11) in the three trays. The humidity actually attained was determined by drawing a measured volume of the conditioned air through two absorption tubes containing sulphuric acid and pumice. The volume of air was measured by a standardized Boys gas meter and the necessary corrections made for temperature, etc.

The turntable consisted of two metal plates fastened to a vertical shaft, the upper plate carrying two rows of hooks, at different levels, and the lower plate one row. This unit was manipulated from outside the cabinet and it could be moved up and down as well as rotated, so that any hook could be brought opposite the balance hanger. A small manipulator, similar to the rider carrier on a balance, fastened to the side of the cabinet, was used to transfer the pieces from the turntable to the balance and *vice versa*. With this equipment over 90 test pieces could be conditioned at one time.

The test pieces were allowed to remain in the chamber until they had reached equilibrium as determined by weighing. In order to weigh the pieces without removing them from the humidostat, a Jolly balance of the Cenco Precision type was employed. From the bottom of the balance spring a straight piece of aluminium wire with a small hook at the lower end extended down into the cabinet through a small hole in the lid. This hole was stoppered when the balance was not in use. The spring extension of the balance is measured by increasing the length of the telescoping stand, and reading the increase on a vernier scale. By using a light steel spring, protected from air currents by a celluloid guard, it was possible to weigh the pieces to the nearest two milligrams.

As explained previously, the dry weight of the treated pieces, over sulphuric acid, was obtained first. The sulphuric acid in the glass trays was then removed and replaced with a saturated solution of lithium chloride (relative humidity 15% (11); actually 11.5 in these tests). All of the test pieces were then reweighed and some of them tested for inflammability when they reached equilibrium. Other saturated salt solutions of progressively increasing vapor pressures were used in turn until the test pieces had attained a moisture content at which they would no longer burn. By this procedure the dry weight of the pieces, the weight of the chlorate absorbed, and the moisture content at each relative humidity was obtained. The large number of test pieces weighed at the low relative humidities gave reliable averages for the moisture content where the weight increases were small. At high relative humidities, when fewer test pieces remained, the weight increases were correspondingly greater and fewer pieces were necessary to attain the same relative precision.

In developing an apparatus for testing inflammability it was found that cloth and paper, treated with sodium chlorate, and dried, could be ignited by dropping a weight on the material. This modified fall-hammer test

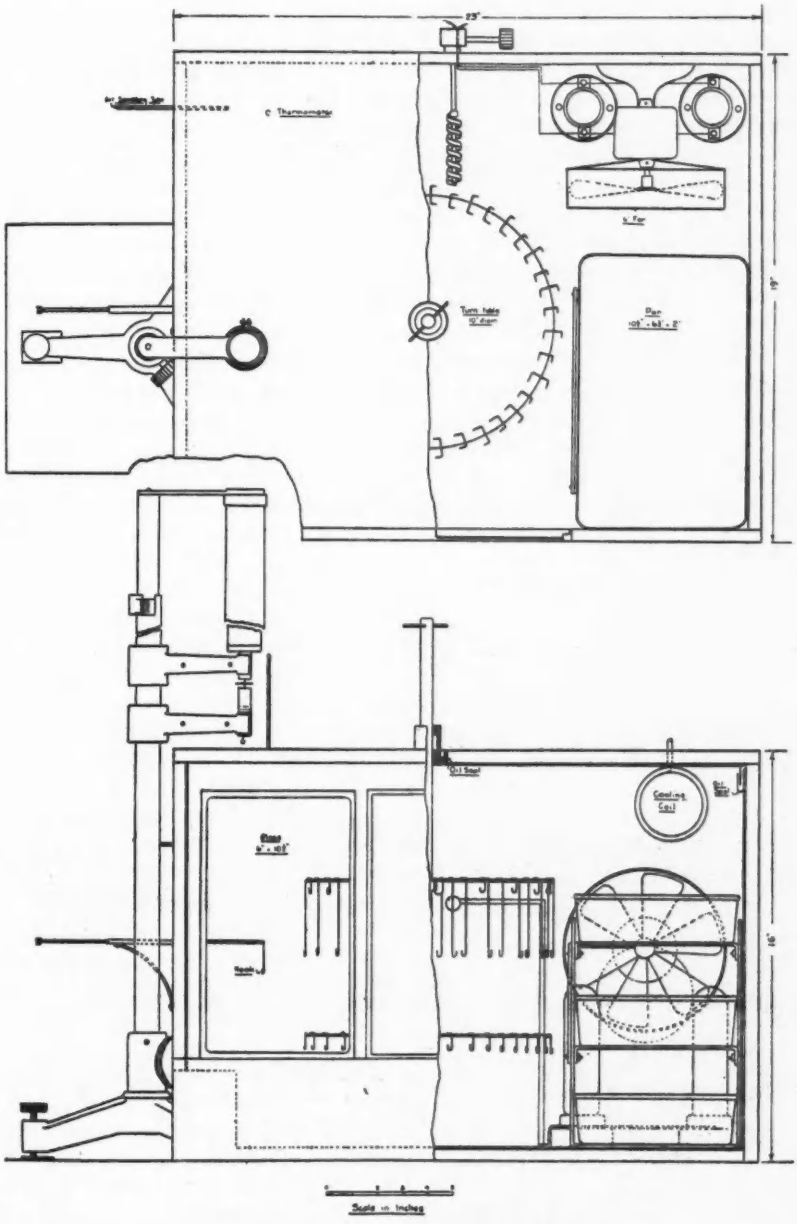


FIG. 1. *Humidostat for conditioning test materials.*

would have required quite elaborate apparatus, however, to test the fire hazard of samples conditioned at different relative humidities. Considerable time is required to establish the minimum height the hammer must fall to explode the material, and during this time the test piece would have changed in moisture content if the apparatus were set up in an ordinary room. Construction of a humidostat for this apparatus would have been possible, but as each combustion would have altered the temperature and humidity conditions temporarily the carrying out of an extensive series of tests would have been time-consuming in the extreme. It was consequently considered desirable to devise a test that could be conducted so rapidly that the material would not change significantly in moisture content while being tested under ordinary laboratory conditions.

The apparatus finally designed for this purpose was essentially an induction coil and spark gap. The test piece, held in a suitable clip, was placed between the electrodes, and the spark permitted to pass through the material for a fixed period. The electrodes were held about ·1 cm. apart, and the current used was sufficient to burn a hole 2 to 3 mm. in diameter, in untreated cloth, in five seconds. A drawing of the complete apparatus which consisted of a 110- to 18-volt step-down transformer, an induction coil, a switch, and a spark gap enclosed in a combustion chamber, is shown in Fig. 2.

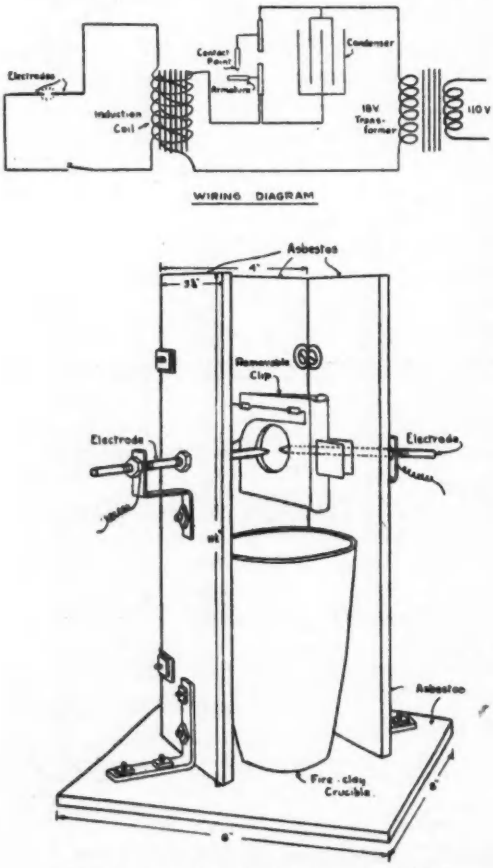


FIG. 2. *Apparatus for testing combustibility.*

A criterion of what constituted a fire hazard had now to be established. In untreated material, regardless of the relative humidity at which it was conditioned, the spark usually burnt a hole 1 to 2 mm. in diameter in about two seconds. This hole would increase in diameter as the spark continued and after five seconds the material would usually be ignited and

would then burn slowly with a free flame. Obviously the small area traversed by the spark was no longer at the moisture content at which it left the conditioning chamber so that any criterion of inflammability had to be taken from the rate of spread in the surrounding material. The inflammability of the treated material was finally classified into three groups as follows:—

1. *Non-hazardous.*—No spontaneous spread of flame when subjected to a spark of five seconds' duration, the burnt hole being of similar size, or smaller, than that burnt in untreated material by a five-second spark.

2. *Doubtful hazard.*—Hole burnt by a five-second spark larger than that obtained in untreated material, with occasional spontaneous spread in a few of the pieces.

3. *Hazardous.*—Material in which flame spread spontaneously after ignition by a spark of less than five seconds' duration.

Plate 1 shows the holes burnt in pieces of cloth and filter paper which have been (a) untreated; (b) treated with an oxidizing agent and are considered a doubtful hazard, since spontaneous spread is quite common in test pieces having a hole of this size from a five-second spark; and (c) treated with an oxidizing agent plus a protecting agent and are considered safe. Obviously hazardous material could not be photographed as it was completely burnt.

Experiments with Sodium Chlorate

In the first experiment, test pieces, cut from cloth and filter paper, were soaked in 10, 20, 30, 40 and 50% sodium chlorate solutions, dried over sulphuric acid, and then conditioned at 25° C. at the relative humidity existing over the various saturated solutions listed in Table I. This table gives two values for the relative humidity; that given in the International Critical Tables (11) and the average values as actually determined in these experiments. These agree quite closely in most cases, but where they do not agree the experimentally determined values are believed to represent the conditions existing in these experiments. The relative humidity maintained by the various solutions at 25° C. is not always given in the International Critical Tables, so the temperature to which the listed values are appropriate is also given in Table I.

TABLE I

RELATIVE HUMIDITY OVER VARIOUS SATURATED SALT SOLUTIONS

Salt	Inter. crit. tables		Experimental	
	Temp. ° C.	R.H. %	Temp. ° C.	R.H. %
$LiCl . H_2O$	20	15	25	11.5
$CaCl_2 . 6H_2O$	24.5	31	25	29
$K_2CO_3 . 2H_2O$	24.5	43	25	43
$Na_2Cr_2O_7 . 2H_2O$	20	52	25	53
NH_4NO_3	25 (approx.)	62 (approx.)	25	61
NH_4Cl and KNO_3	25	71.2	25	65.5
$(NH_4)_2SO_4$	25	81.1	25	78

KEY TO PLATE I

1. Holes burnt in untreated cloth by a spark of five seconds' duration.

2. Holes burnt in untreated filter paper by a spark of five seconds' duration.

Note small holes and large darkened area due to atmospheric oxidation.

3. Holes burnt in cloth soaked in sodium chlorate and conditioned at a relative humidity at which it is a doubtful hazard. Spark of five seconds' duration.

4. Holes burnt in filter paper soaked in sodium chlorate and conditioned at a relative humidity at which it is a doubtful hazard. Spark of five seconds' duration.

Note larger holes with almost complete absence of darkening from atmospheric oxidation.

5. Holes burnt in cloth soaked in sodium chlorate and conditioned at a relative humidity at which it is not a fire hazard. Spark of five seconds' duration.

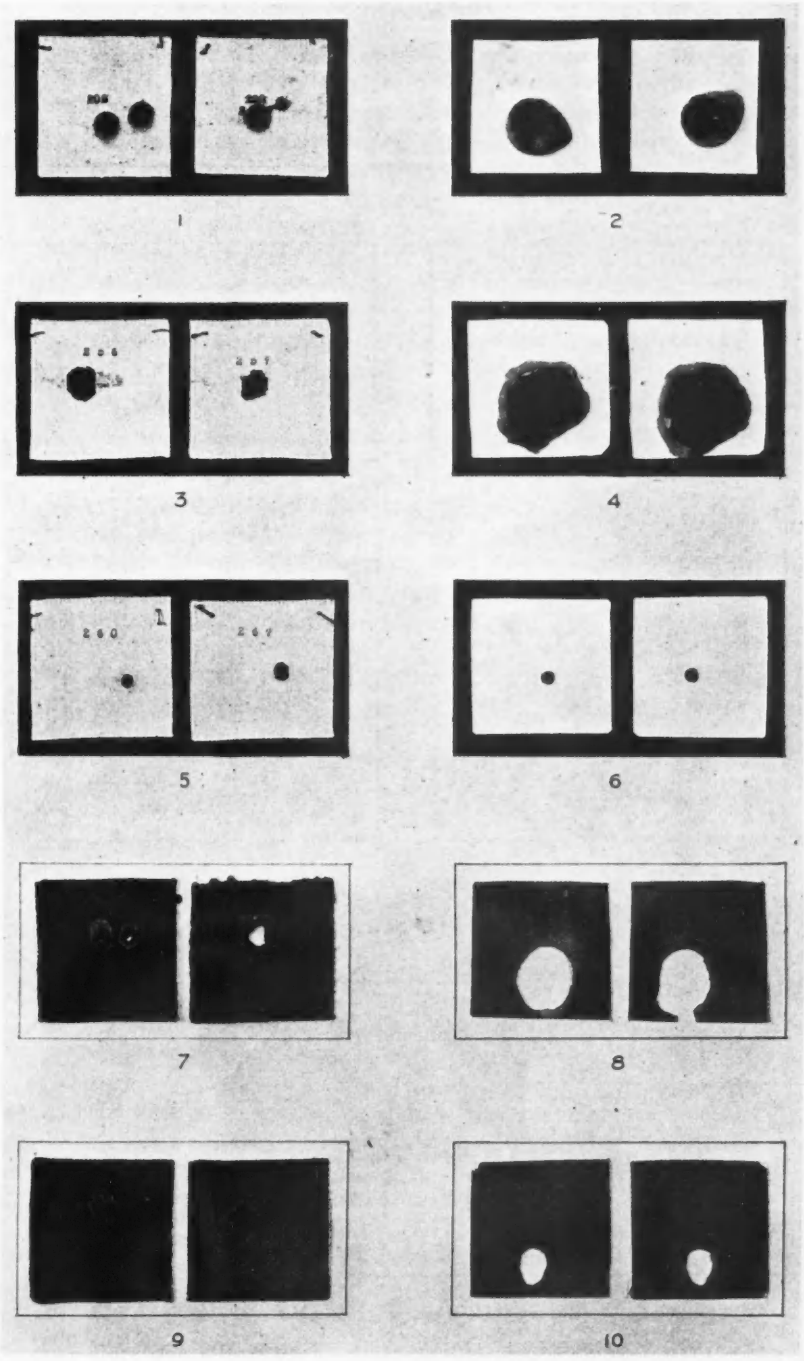
6. Holes burnt in filter paper soaked in sodium chlorate and conditioned at a relative humidity at which it is not a fire hazard. Spark of five seconds' duration.

7. As in 3, but soaked in sodium dichromate.

8. As in 4, but soaked in sodium dichromate.

9. As in 5, but soaked in sodium dichromate.

10. As in 6, but soaked in sodium dichromate.



Showing test pieces of varying degrees of combustibility.

The amount of sodium chlorate taken up by the test pieces varied from about 13% to about 82% of the dry weight of the cloth or filter paper. Fig. 3 A shows that there is an almost linear relation between the percentage of sodium chlorate taken up by the test pieces, and the concentration of the solution in which they were soaked. In every case the filter paper held more salt than the cloth.

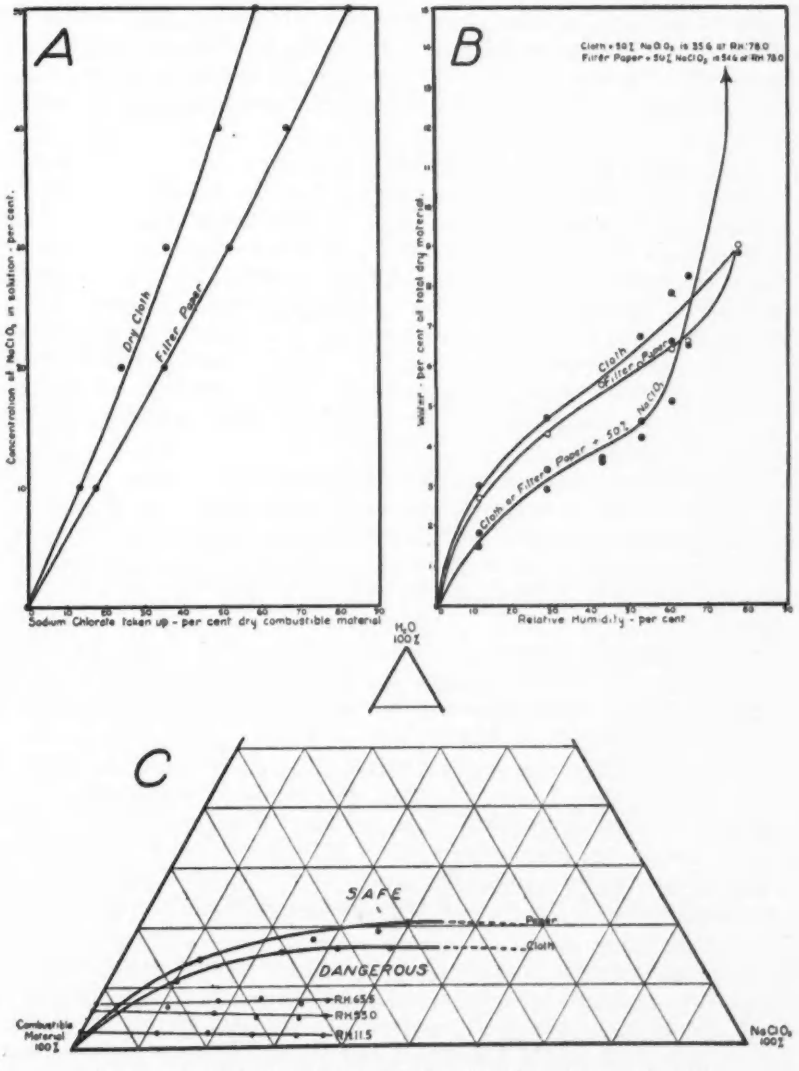


FIG. 3. *Properties of test materials treated with sodium chlorate solutions.*

Fig. 3 B shows the amount of moisture taken up by untreated cloth and filter paper, and also the moisture taken up by the same material after treatment in 50% sodium chlorate, when exposed to atmospheres of different relative humidity. In this figure the moisture content is expressed as a percentage of the weight of the total dry material, regardless of whether it was cloth only, or cloth and sodium chlorate. It is evident from the curves, that sodium chlorate does not take up moisture as readily as cloth, the curve for the treated pieces being below that of the untreated. This applies to all relative humidities below 75%. At this point the vapor pressure of the atmosphere is equal to the vapor pressure of a saturated solution of sodium chlorate (11) and higher relative humidities result in enormous increases in the moisture content of the treated material.

It was found that the test pieces soaked in any of the solutions of sodium chlorate were hazardous at any relative humidity below 75%. Material soaked in a 10% solution seemed to be a little less combustible than that soaked in more concentrated solutions. As would be expected, the filter paper test pieces burned more readily than the cloth. At relative humidities above 75% none of the test pieces would burn at all, regardless of the concentration of the solution in which the pieces had been soaked, and the class of combustible material. The reason for this is evident, since at relative humidities below 75% the moisture content of the material was less than 10%, while test pieces allowed to come to equilibrium at higher humidities contained over 35% moisture.

Although these results show the influence of relative humidity on the combustibility of sodium chlorate-organic matter mixtures, they give no information as to the minimum moisture content required to protect the material. Thus the moisture content of material treated with sodium chlorate increased sharply from about 10% at relative humidities below 75%, to over 35% at humidities just above 75%. The minimum moisture content required for protection must therefore be between 10% and 35%. It is important to know this value accurately, since it would enable the amount of calcium chloride or other water-absorbing substance of known water-holding capacity, required for protection, to be calculated.

In order to obtain this information a number of test pieces were prepared as before and placed in a saturated atmosphere. These pieces were not allowed to come to equilibrium, as in the previous experiment. Instead, one or two of the pieces were weighed at frequent intervals to determine their moisture content, and then removed for the combustibility test. This was continued until the material had taken up sufficient moisture to remove the fire hazard.

The results showed that the amount of moisture required to protect the test pieces varied somewhat with the proportions of the combustible material and of sodium chlorate they contained. In order to represent these results graphically a triangular diagram, shown in Fig. 3 C, has been employed. To use this type of chart it is necessary to express the amount of each com-

ponent as a percentage of the whole, so that the sum of the percentages is equal to one hundred. The triangle is equilateral, the distance from the centre of one side to the opposite corner representing 100. The corners of the triangle represent the three individual components, the sides represent mixtures of two components, and since every point within the triangle has the property that the sum of the perpendiculars from this point to the sides is equal to 100, it is evident that the composition of a three-compound system can be represented by fixing a point within the triangle. The fractional amount of a given component is then represented by the perpendicular distance of the point from the side of the triangle opposite the corner representing this component.

The upper curve in Fig. 3 C divides the filter paper-sodium chlorate mixtures into those which contain sufficient moisture to be safe, and those which do not. Points in the area above this curve represent systems that are safe while points in the area below the curve represent systems that are dangerous. The lower curve gives the same information for cloth, a less combustible substance. Tests made with leaves that had been treated with sodium chlorate indicated that they have a combustibility intermediate between the curves obtained with cloth and filter paper, but it was impossible to get reliable data with such material.

In order to extend the curves over as wide a range as possible, a few pieces of the test materials were soaked in a saturated sodium chlorate solution. This resulted in the dry material containing as high as 52% sodium chlorate. Higher percentages of salt would not adhere to the cloth when dry. The entire range of practical importance has been covered, however, and the curve has been extrapolated, as a dotted line, a short distance beyond the experimental points.

The straight lines in the lower left hand corner of the Fig. 3 C, represent the amount of water taken up by the different systems at relative humidities below 75%. No data are shown for the relative humidities above 75% as the material containing sodium chlorate took up so much moisture that some of the resulting solution drained off the pieces, making the weights unreliable. It is evident, however, that at all ordinary atmospheric humidities there is not sufficient water retained by sodium chlorate-organic matter mixtures, to provide protection.

The curves shown in Fig. 3 C enable the approximate amount of any water-absorbing chemical that has to be added to sodium chlorate to remove the fire risk when the latter is mixed with organic material, to be estimated. Examination of the curves also reveals that the amount of moisture-retaining chemical required for protection will depend on the relative amount of combustible material present. In practice the amount of herbicide that may come in contact with organic material is wholly uncontrollable. The only factor that can be controlled is the composition of the herbicide. The latter must therefore contain enough water-absorbing chemical to provide protection regardless of the amount of organic matter present.

The foregoing curves show that when organic matter becomes contaminated with a herbicide composed of sodium chlorate and a water-absorbing chemical in fixed proportions, the fire risk tends to decrease rather than increase if more herbicide is added. The reason for this is that each successive increment of sodium chlorate added to the organic material requires a smaller increment of water for protection.

For example, consider a mixed herbicide composed of two-thirds sodium chlorate and one-third anhydrous calcium chloride. At relative humidities as low as 22% this amount of calcium chloride will retain sufficient moisture to bring the water content of the mixture, on a wet basis, up to about 25%. When organic matter containing 5% moisture (Fig. 3 B) is added to this herbicide the percentage moisture in the resultant mixture will be some intermediate value. According to Fig. 3 C this mixture will not become dangerous unless it has a moisture content less than 20%, as this moisture content protects organic matter-sodium chlorate mixtures of almost any proportion. This moisture content will be reached when about one-quarter of the mixture is organic material. Further additions of organic matter will cause further reduction in the percentage moisture and the mixture will become dangerous. The diluting effect of the non-combustible calcium chloride, apart from its moisture-retaining power, will tend further to reduce the inflammability, but the extent to which this is effective can be determined only by direct experiment. The above reasoning shows, however, that the inflammability increases rather than decreases, within certain limits, as the quantity of the mixed herbicide in the mixture decreases.

Experiments with Sodium Chlorate Plus Protecting Agents

In selecting a salt for admixture with sodium chlorate in order to reduce the fire risk, the choice lies among chemicals which retain moisture and those which reduce the inflammability in other ways. The first type includes such chemicals as calcium chloride, and their efficiency will depend on the amount of water held, the form in which it is held, the vapor pressure of this hydrate, the vapor pressure of a saturated solution of the salt, and the atmospheric humidity to which any contaminated material may be exposed.

The second type will include ammonium phosphate and other chemicals which have been used for fireproofing wood, cloth, etc. The efficiency of these chemicals in reducing the combustibility of organic material will depend on their form of deposition on, and their penetration into, the material, more than upon their deliquescent properties. The special treatments commonly used in applying these materials are obviously impossible with herbicides. Soluble carbonates which decompose at the combustion temperature, with the evolution of carbon dioxide, might also be effective in reducing the fire hazard by checking the spread of flame.

Any non-combustible material mixed with sodium chlorate will reduce the inflammability of contaminated material by dilution regardless of its other properties. The effectiveness of such a substance will depend on the

amount present. Obviously salts of high herbicidal power can economically form a much larger proportion of the herbicide than those that are merely inert material from the toxicity standpoint.

The vapor pressure data for a number of hydrated salts are given in Table II. In this table the vapor pressures have been expressed as the relative humidity at the given temperature. At atmospheric humidities lower than those given in the fourth column, the saturated solution will dry out leaving the crystalline hydrate; and this hydrate will decompose to the next lower hydrate, if one exists, at relative humidities lower than those given in the third column.

TABLE II

VAPOR PRESSURE OF SOME HYDRATED SALTS, AND OF THEIR SATURATED SOLUTIONS

Salt	Water in hydrate, %	Vapor pressure of hydrate expressed as relative humidity at given temperature (1), %	Vapor pressure of saturated solution expressed as relative humidity at given temperature (2), %	Remarks
$NaClO_3$	0	—	75 (20° C.)	
$Ca(ClO_3)_2 \cdot 2H_2O$	14.8	—	—	
$Ba(ClO_3)_2 \cdot H_2O$	5.6	—	—	
$Na_2Cr_2O_7 \cdot 2H_2O$	12.1	—	52 (20° C.)	
$CaCl_2 \cdot 6H_2O$	49.3	22 (25° C.)	31 (24.5° C.)	M.p. of hydrate, 29.9° C.
$Na_2CO_3 \cdot 10H_2O$	62.9	76 (25° C.)	87 (24.5° C.)	M.p. of hydrate, 32–34° C.
$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	47.6	23 (50° C.)	—	
$Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	45.5	26 (20° C.)	—	
$Cr_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	43.2	26 (30° C.)	—	
$CuSO_4 \cdot 5H_2O$	36.0	33 (20° C.)	94 (60° C.)	
$MgCl_2 \cdot 6H_2O$	53.1	4.6 (31.6° C.)	32 (25° C.)	
$FeCl_3 \cdot 6H_2O$	40.0	14 (15° C.)	—	
$Na_2B_4O_7 \cdot 10H_2O$	47.1	49 (20° C.)	—	
$NaOH \cdot H_2O$	31.0	0.6 (25° C.)	—	
$Na_2HPO_4 \cdot 12H_2O$	60.3	78 (25° C.)*	—	*Av. last two values given in tables.
$ZnCl_2$ (lowest hydrate)	—	3.6 (25° C.)	10 (20° C.)	
$ZnSO_4 \cdot 7H_2O$	43.8	57 (25° C.)	90 (20° C.)	

(1) *Data obtained from Vol. VII, Int. Crit. Tables.* (2) *Data obtained from Vols. I and III, Int. Crit. Tables.*

The available data on the properties of the oxidizing agents themselves are given first in Table II. Sodium chlorate does not form a hydrate and it forms a saturated solution only at relative humidities higher than 75%. The higher water content of calcium and barium chlorate is evident, but there are few data available concerning the vapor pressure of these hydrates. Sodium dichromate holds 12.1% of water, and will take up moisture to form a saturated solution at relative humidities higher than 52%. This, together with its higher equivalent weight, indicates that it should be less dangerous than sodium chlorate.

Calcium chloride and sodium carbonate are the two substances most commonly mixed with sodium chlorate in commercial herbicides, and the properties of these salts appear next in the table. Although the carbonate holds a higher percentage of water, it decomposes under ordinary atmospheric conditions, the saturated solution drying out at humidities below 87%, while the decahydrate itself decomposes at humidities below 76% of saturation. On the other hand, solutions of calcium chloride are stable at all relative humidities above 31%, and the hexahydrate exists at humidities as low as 22%.

The other salts listed in Table II represent some of the compounds tested as protecting agents in this investigation. The alums contain about 45% of water and decompose at relative humidities below about 26%. Magnesium chloride holds more water of crystallization than calcium chloride, and this hydrate is stable at lower humidities and higher temperatures than that of the calcium salt. These data indicate that magnesium chloride should be the best protecting agent of the chemicals listed in Table II. The remaining hydrated salts are less promising for they either hold a lower percentage of water or decompose at ordinary atmospheric humidities. Sulphuric acid would be one of the most effective reagents for retaining moisture under ordinary conditions, but unfortunately its admixture with sodium chlorate would result in the formation of chloric acid which decomposes readily, with a consequent reduction in the toxic properties of the herbicide. Many other reagents, commonly used for moisture absorption, are too expensive to be of practical value for this purpose.

The protecting action of these and other salts was determined in the manner previously described for testing the inflammability of sodium chlorate-organic matter mixtures. The salt to be tested was dissolved with the sodium chlorate, in various proportions, in the test solution. By using solutions of different concentrations it was also possible to vary the percentage of organic matter in the test material. Cloth (12-oz. duck) was the principal experimental substance. Initially dried leaves and filter paper were also included as test materials, but these were abandoned as it was found impossible to get quantitative results owing to their disintegration at various stages of the test. Both of these materials, however, appeared to be somewhat more combustible than cloth treated in a similar manner.

The first protecting salt tested was calcium chloride and the results obtained are presented in Table III. This table shows the proportion of anhydrous sodium chlorate used, and the concentration of the mixed salts in the test solution in percentage; *i.e.*, grams of salt mixture per 100 cc. of solution. Under the heading "Composition of test material" the amount of combustible material, salt, and water, have been expressed as a percentage of the whole. The percentage of salt includes both the sodium chlorate and calcium chloride but the percentage of sodium chlorate can be estimated, without serious error, from the proportion of this salt in the test solution.

Table III shows that all material tested at 11.5% relative humidity had a low moisture content and was hazardous. This is to be expected since

$CaCl_2 . 6H_2O$ loses some of its water of crystallization at relative humidities below about 22%. At relative humidities higher than 31%, calcium chloride will exist in the form of a saturated solution, but there does not appear to be a break in the curve at this point, although the percentage of water in the test pieces increases steadily as the relative humidity is raised. Furthermore,

TABLE III

COMBUSTIBILITY OF $NaClO_3$-$CaCl_2$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test
			Combustible material, %	Salt, %	Water, %	
½ $NaClO_3$ ½ $CaCl_2$	60*	11.5	48.2	46.3	5.5	Hazard
		29.0	42.6	40.8	16.6	No hazard
½ $NaClO_3$ ½ $CaCl_2$	40	11.5	62.0	32.6	5.4	Hazard
		29.0	58.8	29.3	11.9	No hazard
		43.0	55.0	28.0	17.0	No hazard
½ $NaClO_3$ ½ $CaCl_2$	20	29.0	73.6	19.1	7.3	Doubtful hazard
		43.0	70.8	18.6	10.6	Doubtful hazard
		53.0	67.6	18.2	14.2	No hazard
¾ $NaClO_3$ ¼ $CaCl_2$	60	11.5	52.4	42.6	5.0	Hazard
		29.0	50.0	39.0	11.0	Doubtful hazard
		43.0	43.5	41.6	14.9	No hazard
¾ $NaClO_3$ ¼ $CaCl_2$	45	11.5	60.4	35.7	3.9	Hazard
		29.0	56.9	34.4	8.7	Hazard
		43.0	52.7	33.1	14.2	Doubtful hazard
		53.0	52.0	30.5	17.5	No hazard
¾ $NaClO_3$ ¼ $CaCl_2$	30	11.5	68.7	27.2	4.1	Hazard
		29.0	68.4	24.6	7.0	Hazard
		43.0	64.5	25.5	10.0	Doubtful hazard
		53.0	61.5	24.9	13.6	Doubtful hazard
¾ $NaClO_3$ ¼ $CaCl_2$	40	29.0	63.1	30.2	6.7	Hazard
		43.0	60.3	30.1	9.6	Hazard
		53.0	58.3	29.1	12.6	Doubtful hazard
		61.0	56.0	28.4	15.6	No hazard
¾ $NaClO_3$ ¼ $CaCl_2$	20	29.0	75.4	19.2	5.4	Hazard
		43.0	74.1	18.8	7.1	Hazard
		53.0	72.0	18.9	9.1	Doubtful hazard
		61.0	68.6	17.7	13.7	Ext. doubtful hazard
¾ $NaClO_3$ ¼ $CaCl_2$	25	11.5	73.1	23.8	3.1	Hazard
		29.0	71.5	23.4	5.1	Hazard
		43.0	69.2	23.6	7.2	Hazard
		53.0	68.9	22.0	9.1	Hazard
		61.0	65.7	21.2	13.1	Doubtful hazard
¾ $NaClO_3$ ¼ $CaCl_2$	12.5	43.0	81.2	12.4	6.4	Doubtful hazard
		53.0	79.8	12.0	8.2	Doubtful hazard
		61.0	77.6	11.6	10.8	No hazard

**Part of material undissolved.*

test material classed as "hazard" and "doubtful hazard" at 29% relative humidity frequently shows no significant decrease in combustibility when the humidity is raised to 43%. Comparison of tests in the same group at the same relative humidity shows, as pointed out earlier, that with the exception of the lowest values the combustibility tends to increase as the percentage of the mixed salt, sodium chlorate and calcium chloride, in the test material decreases. The inflammability naturally increases as the proportion of calcium chloride in the sodium chlorate is reduced. The minimum amount of calcium chloride required for protection will depend on the atmospheric humidity to which the herbicide is exposed. Thus equal parts of sodium chlorate and anhydrous calcium chloride can be considered safe at all relative humidities above 43%; two parts of sodium chlorate and one part of anhydrous calcium chloride will be comparatively safe at all humidities above about 53%, while four parts of sodium chlorate to one of calcium chloride will be safe only when the relative humidity is above about 60%. The effect of these large proportions of calcium chloride on the toxic properties of the herbicide will be discussed later.

TABLE IV

COMBUSTIBILITY OF $NaClO_3$-$MgCl_2$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test
			Combustible material, %	Salt, %	Water, %	
⅔ $NaClO_3$ / ⅓ $MgCl_2$	60	11.5	41.2	49.0	9.8	No hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	40	11.5	55.0	37.0	8.0	No hazard
		29.0	51.2	34.0	14.8	No hazard
		43.0	49.2	32.0	18.8	No hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	20	11.5	72.7	22.0	5.3	Doubtful hazard
		29.0	72.2	19.4	8.4	No hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	45	11.5	55.8	37.5	6.7	Doubtful hazard
		29.0	53.8	35.0	11.2	No hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	30	11.5	67.6	27.6	4.8	Doubtful hazard
		29.0	63.0	28.4	8.6	Doubtful hazard
		43.0	61.7	26.3	12.0	No hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	40	29.0	61.5	31.3	7.2	Doubtful hazard
		43.0	60.6	29.6	9.8	Doubtful hazard
		53.0	58.1	28.7	13.2	Doubtful hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	20	29.0	71.8	22.0	6.2	Hazard
		43.0	69.9	22.4	7.7	Doubtful hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	25	29.0	73.0	22.0	5.0	Hazard
		43.0	71.6	21.3	7.1	Doubtful hazard
		53.0	66.0	24.5	9.5	Doubtful hazard
⅔ $NaClO_3$ / ⅓ $MgCl_2$	12.5	29.0	81.0	13.8	5.2	Doubtful hazard
		43.0	80.3	13.0	6.7	Doubtful hazard
		53.0	78.9	12.6	8.5	No hazard

Magnesium chloride was the next salt considered since the data presented in Table II indicated that it should be the best protecting agent of the hydrated salts listed in that table. The data are presented in Table IV in the same form as in Table III. It is again evident that, with the exception of the mixtures containing the smallest amount of the mixed salt, the fire hazard decreases as the proportion of mixed herbicide increases. These experiments bear out the earlier indications that magnesium chloride is a better protecting agent than calcium chloride. Mixtures of equal parts of sodium chlorate and anhydrous magnesium chloride are safe at 29% relative humidity, and even mixtures of two parts of sodium chlorate to one of magnesium chloride are relatively safe at this humidity, and entirely safe above 43%. Mixtures containing lower proportions of magnesium chloride are a doubtful hazard at 53% humidity, the highest value used in this experiment.

Mixtures of sodium chlorate and sodium carbonate are used as commercial herbicides, and this latter salt was the next to receive consideration. The results obtained are presented in Table V. They show that sodium carbonate

TABLE V

COMBUSTIBILITY OF $NaClO_3$-Na_2CO_3-CLOTH, AND $NaClO_3$-NaOH-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test	Remarks
			Combustible material, %	Salt, %	Water, %		
½ $NaClO_3$ ½ Na_2CO_3	40	11.5	73.6	24.4	2.0	Hazard	Spontaneous spread without flame but with numerous sparks
		29.0	71.3	26.6	2.1	Hazard	
		43.0	69.4	24.7	5.9	Hazard	
		53.0	68.4	24.0	7.6	Doubtful hazard	Some ppt. in soln.
⅔ $NaClO_3$ ⅓ Na_2CO_3	60	11.5	58.2	40.4	1.4	Hazard	Quite heavy ppt. No flame (sparks)
		29.0	56.8	40.4	2.8	Hazard	
⅓ $NaClO_3$ ⅔ Na_2CO_3	30	11.5	67.9	30.3	1.8	Hazard	Slight ppt. No flame but sparks
		43.0	66.7	27.6	5.7	Hazard	
		53.0	65.7	27.3	7.0	Hazard	
½ $NaClO_3$ ½ NaOH	40	11.5	—	—	(2.7)	Hazard	Test pieces swelled in this soln., and disintegrated, making dry weight unreliable
		29.0	—	—	(11.1)	No hazard	
		43.0	—	—	(14.1)	No hazard	
½ $NaClO_3$ ½ NaOH	20	11.5	(75.7)	(21.7)	(2.6)	Hazard	Weights given but are not considered reliable due to swelling
		29.0	(69.6)	(21.8)	(8.6)	Doubtful hazard	
		43.0	(68.6)	(21.6)	(9.8)	No hazard	
½ $NaClO_3$ ½ NaOH	30	11.5	(68.4)	(30.0)	(1.6)	Hazard	Weights given but are not considered reliable due to swelling
		29.0	(66.3)	(26.9)	(6.8)	Hazard	
		43.0	(64.5)	(26.2)	(9.3)	Hazard	
		53.0	(62.8)	(26.4)	(10.8)	Hazard	

retains very little moisture and is of little value as a protecting agent. These experiments covered mixtures composed of one-half and one-third anhydrous sodium carbonate only, and as these were a distinct hazard, lower proportions of carbonate were not tested.

Although sodium carbonate was of little value as a protecting agent, judging from the rapid spread of the burnt area, it did have an effect on the inflammability, as none of the pieces burned with a free flame. However, in view of the large number of sparks developed, and the rapid spread of the burnt area, the lack of flame cannot be considered a practical advantage. In any event, sodium carbonate appears to be inferior to calcium or magnesium chloride for admixture with sodium chlorate as a safeguard against fire.

The data given in Table II show that sodium hydroxide retains about 31% of water at very low relative humidities. Under atmospheric conditions, however, most of this substance would be converted to sodium carbonate. Its value as a protecting agent was nevertheless determined using the method employed in testing the other salts. The data obtained are presented in Table V. The test material swelled considerably while being treated in the caustic-chlorate solutions, and a considerable amount of carbonate was formed on the material during subsequent conditioning. The quantitative data, concerning the composition of the material, are consequently only approximate. The combustion test shows that mixtures of one-half sodium chlorate and one-half sodium hydroxide are comparatively safe at relative humidities above 29%, and completely safe at humidities above 43%. Mixtures containing only one-third sodium hydroxide, however, are hazardous at all humidities up to 53%, the highest value tested. Comparison of the protecting action of sodium carbonate, formed on the material by treatment in alkali and subsequent exposure to the air, with that of sodium carbonate applied in solution, suggests that the former is more effective. It must be remembered, however, that the proportion of carbonate is somewhat higher in the material treated with sodium hydroxide than in the material treated with sodium carbonate directly.

Table VI shows the results obtained with three alums and with chromium nitrate. It was found impossible to make 40% solutions of salt mixtures containing one-half aluminium potassium or aluminium ammonium alum, as some of the material would not dissolve. The solution resulting from an attempt to prepare a 40% concentration was tested, however, and it is evident that the amount of alum which did dissolve had little protective action. Mixtures composed of two-thirds sodium chlorate and one-third alum were also hazardous although they dissolved to form a 30% solution. As these salts showed no promise as protecting agents no further tests were made.

The results obtained with chrome alum show that none of the material was dangerous even at relative humidities of 11.5%. It was observed, however, that the test material gained but little weight as the humidity was increased, in fact in some cases weight was lost. Furthermore, the tensile strength of

the material was reduced and tests for the chlorate ion showed that most of it had disappeared. These observations suggested that the chromium ion tended to catalyze the oxidation of the organic material by the sodium chlorate.

TABLE VI

COMBUSTIBILITY OF $NaClO_3$-$Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$-CLOTH, $NaClO_3$-$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$-CLOTH, $NaClO_3$-$Cr_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$-CLOTH, AND $NaClO_3$-$Cr(NO_3)_3$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test	Remarks
			Combustible material, %	Salt, %	Water, %		
½ $NaClO_3$ ½ $Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	40	11.5	71.8	26.2	2.0	Hazard	Slight ppt.
		29.0	70.6	25.4	4.0	Hazard	
		43.0	68.8	25.7	5.5	Hazard	
½ $NaClO_3$ ½ $Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$	30	11.5	74.4	24.9	0.7	Hazard	
		29.0	73.2	22.6	4.2	Hazard	
		43.0	71.7	22.6	5.7	Hazard	
½ $NaClO_3$ ½ $Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	40	11.5	73.6	24.4	2.0	Hazard	Heavy precipitate
		29.0	72.0	22.5	5.5	Hazard	
		43.0	69.5	(24.9)	(5.6)	Doubtful hazard	
½ $NaClO_3$ ½ $Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	30	11.5	76.8	21.0	2.2	Hazard	
		29.0	74.6	21.4	4.0	Hazard	
		43.0	72.4	22.0	5.6	Doubtful hazard	
½ $NaClO_3$ ½ $Cr_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	40	11.5	(71.3)	(26.8)	(1.9)	No hazard	Pieces lost weight, and had much lower tensile strength after washing and standing
		29.0	(71.5)	(25.0)	(3.5)	No hazard	
		43.0	(71.0)	(24.8)	(4.2)	No hazard	
½ $NaClO_3$ ½ $Cr_2SO_4(NH_4)_2SO_4 \cdot 24H_2O$	30	11.5	(76.6)	(21.4)	(2.0)	Doubtful hazard	Pieces lost weight, and had much lower tensile strength after washing and standing
		29.0	(74.8)	(21.8)	(3.4)	Doubtful hazard	
		43.0	(73.2)	(22.5)	(4.3)	No hazard	
½ $NaClO_3$ ½ $Cr(NO_3)_3$	40	11.5	(67.3)	(29.6)	(3.1)	Doubtful hazard	Pieces rotten
		29.0	(67.4)	(27.5)	(5.1)	No hazard	
		43.0	(66.5)	(27.4)	(6.1)	No hazard	
½ $NaClO_3$ ½ $Cr(NO_3)_3$	30	11.5	(72.9)	(24.6)	(2.5)	Doubtful hazard	Pieces rotten
		29.0	(71.6)	(25.1)	(3.3)	Doubtful hazard	
		43.0	(70.6)	(24.0)	(5.4)	Doubtful hazard	
½ $NaClO_3$ ½ $Cr(NO_3)_3$	25	11.5	(74.8)	(23.0)	(2.2)	Hazard	
		29.0	(74.6)	(21.5)	(3.9)	Doubtful hazard	
		43.0	(74.8)	(21.0)	(4.2)	Doubtful hazard	

Tests were made with chromium nitrate to check this point, with similar results. Determination of the hydrogen ion concentration in these solutions showed that they were of pH approximately 2.0 and as this degree of acidity would cause the formation of chloric acid, which decomposes in the presence of organic matter, the disappearance may be explained by the acidity of the solution rather than by the presence of the chromium. In any event, such salts could not be used as protecting agents in chlorate herbicides, since they destroy the toxic compound.

The results obtained with copper sulphate, ferric chloride, and aluminium chloride, are presented in Table VII. It seemed from the point of view of

TABLE VII

COMBUSTIBILITY OF $NaClO_3$-$CuSO_4$-CLOTH, $NaClO_3$-$FeCl_3$-CLOTH, AND $NaClO_3$-$AlCl_3$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test	Remarks
			Combustible material, %	Salt, %	Water, %		
½ $NaClO_3$ ½ $CuSO_4$	40	11.5	60.0	34.0	6.0	Hazard	
		29.0	62.7	32.4	4.9	Hazard	
		43.0	60.3	33.1	6.6	Hazard	
		53.0	64.8	26.5	8.7	Hazard	
		61.0	64.2	27.5	8.3	Hazard	
		71.0	Not weighed			No hazard	
½ $NaClO_3$ ½ $CuSO_4$	30	11.5	70.5	27.0	2.5	Hazard	
		29.0	69.3	26.0	4.7	Hazard	
		43.0	67.4	26.0	6.6	Hazard	
		61.0	65.6	26.0	8.4	Hazard	
		71.0	Not weighed			Doubtful hazard	
½ $NaClO_3$ ½ $FeCl_3$	40	11.5	(64.3)	(32.1)	(3.6)	Doubtful hazard	Soln. decomposed having strong odor of chlorine
		29.0	(62.5)	(26.6)	(10.9)	Doubtful hazard	
		43.0	(60.8)	(30.2)	(9.0)	No hazard	
½ $NaClO_3$ ½ $FeCl_3$	30	11.5	(71.6)	(25.5)	(2.9)	Doubtful hazard	Soln. decomposed having strong odor of chlorine
		29.0	(69.3)	(25.8)	(4.9)	Doubtful hazard	
		43.0	(70.8)	(23.2)	(6.0)	Doubtful hazard	
½ $NaClO_3$ ½ $AlCl_3$	40	11.5	(58.4)	(38.8)	(2.8)	No hazard	Soln. decomposed giving off Cl_2 gas and leaving a white ppt.
		29.0	(57.8)	(37.2)	(5.0)	No hazard	
½ $NaClO_3$ ½ $AlCl_3$	30	11.5	(70.0)	(26.4)	(3.6)	Doubtful hazard	Soln. decomposed giving off Cl_2 gas but solution remained clear
		29.0	(68.4)	(25.6)	(6.0)	Doubtful hazard	
		43.0	(66.7)	(25.1)	(8.2)	No hazard	

herbicidal value that salts such as copper sulphate, which are quite toxic to plants, might be used in a mixed herbicide more profitably than salts such as calcium chloride which are less toxic. A herbicide composed of equal parts of sodium chlorate and copper sulphate, however, was found in these tests to be hazardous at relative humidities as high as 61%. These results show that copper sulphate is of little value in reducing the inflammability of sodium chlorate-organic matter mixtures even when it is present in large proportions.

Ferric chloride and aluminium chloride are both hydrated salts and were therefore tested for their protective action. When these substances were dissolved in the solution containing the sodium chlorate, decomposition set in immediately with the evolution of chlorine. Both salts made the solution quite acidic. Further decomposition of the chlorate took place after the test pieces had been treated, and the reduced combustibility of material treated in solutions containing the above salts can be explained by the disappearance of the chlorate ion. In consequence neither ferric nor aluminium chloride can be used as protecting agents in chlorate herbicides.

The next series of substances tested consists of salts, which in addition to their capacity for retaining moisture are known to exert a definite fire-preventing action. These include sodium borate, sodium stannate, sodium and ammonium acid phosphate, zinc chloride and zinc sulphate. Ammonium phosphate and zinc chloride, applied under pressure, have been used quite extensively for fireproofing wood. Sodium stannate has been used for fireproofing cloth, the material being treated with a sodium stannate solution first, and the metallic ion subsequently precipitated on the material by treatment with another solution. Obviously such treatments cannot be employed to lower the combustibility of organic material contaminated with sodium chlorate. The only test of these materials applicable to field conditions is to mix the reagent with the sodium chlorate and test its effect on the combustibility when applied in this manner.

The results obtained with the above salts are presented in Table VIII. Sodium borate and the two phosphate salts were too insoluble at ordinary temperatures in the chlorate solutions to permit high proportions of these salts to be used. Even in the proportions used considerable amounts of undissolved material remained and it is evident that these substances exerted little protective action. Sodium stannate like sodium carbonate seemed to arrest the formation and spread of flame, but the burnt area spread rapidly without flame and the material was considered quite hazardous at low humidities. The zinc salts in addition to their water-retaining and fire-preventing properties, are quite good herbicides. In these tests, however, they seemed not to affect the combustibility to any extent, and are consequently of little value for admixture with sodium chlorate with the object of reducing the fire risk.

Soluble arsenicals and ammonium thiocyanate are known to be effective herbicides, and although none of these salts would be expected to reduce the combustibility of organic material significantly, they could form a much larger

TABLE VIII

COMBUSTIBILITY OF $NaClO_3$-$Na_2B_4O_7$-CLOTH, $NaClO_3$-Na_2SnO_3-CLOTH, $NaClO_3$-Na_2HPO_4-CLOTH, $NaClO_3$-$ZnCl_2$-CLOTH AND $NaClO_3$-$ZnSO_4$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Results of combustion test	Remarks
			Combustible material, %	Salt, %	Water, %		
½ $NaClO_3$ ½ $Na_2B_4O_7$	30	11.5	74.8	23.5	1.7	Hazard	Heavy pp't. from this test sol'n.
		29.0	74.1	22.2	3.7	Hazard	
		43.0	73.5	21.0	5.5	Hazard	
½ $NaClO_3$ ½ Na_2SnO_3	40	11.5	61.7	35.8	2.5	Hazard	Slight precipitate
		29.0	60.0	35.2	4.8	Doubtful hazard	
		43.0	59.6	33.5	6.9	Doubtful hazard	
½ $NaClO_3$ ½ Na_2SnO_3	30	11.5	69.7	27.6	2.7	Doubtful hazard	Slight precipitate
		29.0	68.6	25.6	5.8	Doubtful hazard	
		43.0	67.8	25.2	7.0	Doubtful hazard	
½ $NaClO_3$ ½ Na_2HPO_4	30	11.5	72.8	25.4	1.8	Hazard	Heavy precipitate
		29.0	70.5	25.0	4.5	Hazard	
		43.0	69.6	25.4	5.0	Hazard	
½ $NaClO_3$ ½ $(NH_4)_2HPO_4$	30	11.5	73.7	25.0	1.3	Hazard	Heavy precipitate from this test solution
		29.0	72.3	24.6	3.1	Hazard	
		43.0	72.3	22.8	4.9	Hazard	
½ $NaClO_3$ ½ $ZnCl_2$	40	11.5	64.4	32.6	3.0	Hazard	
		29.0	63.3	31.0	5.7	Hazard	
½ $NaClO_3$ ½ $ZnCl_2$	60	11.5	57.2	40.4	2.4	Hazard	
		29.0	57.7	37.4	4.9	Hazard	
½ $NaClO_3$ ½ $ZnCl_2$	30	11.5	72.1	25.6	2.3	Hazard	
		29.0	70.9	24.5	4.6	Hazard	
½ $NaClO_3$ ½ $ZnSO_4$	40	11.5	64.5	33.8	1.7	Hazard	$ZnSO_4$ seemed to cut down intensity of flame but did not remove the fire risk
		29.0	63.1	32.8	4.1	Hazard	
		43.0	63.2	32.8	4.0	Doubtful hazard	
½ $NaClO_3$ ½ $ZnSO_4$	30	11.5	70.0	28.8	1.2	Hazard	
		29.0	68.7	27.4	3.9	Hazard	
		43.0	67.3	27.8	4.9	Hazard	

proportion of the herbicide without significantly reducing the toxicity. The protective action of arsenic pentoxide, sodium arsenite, sodium arsenate and ammonium thiocyanate, was therefore tested and the results obtained are presented in Table IX. Arsenic pentoxide and ammonium thiocyanate made the sodium chlorate solution quite acidic and partial decomposition of the chlorate resulted. This effect eliminates the possibility of using them as

protective agents. Mixtures composed of one-half sodium arsenite or sodium arsenate with sodium chlorate, when applied to organic material, remained a doubtful fire risk at relative humidities of 43%. The practical value of such mixtures is not likely to be great, in view of the fact that, although the combustibility is reduced as compared with pure sodium chlorate, a fire risk still exists, and in addition the herbicide has been made highly poisonous to livestock by the addition of the arsenical.

TABLE IX

COMBUSTIBILITY OF $NaClO_3$-As_2O_3-CLOTH, $NaClO_3$-Na_2HAsO_3-CLOTH, $NaClO_3$-Na_2HAsO_4-CLOTH, AND $NaClO_3$-NH_4CNS-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Results of combustion test	Remarks
			Combustible material, %	Salt, %	Water, %		
½ $NaClO_3$ ½ As_2O_3	40	11.5	(67.1)	(30.8)	(2.1)	Hazard	All of these solutions decomposed as shown by the extreme bleaching and reduction in strength of the test pieces
		29.0	(65.6)	(30.3)	(4.1)	Hazard	
		43.0	(65.5)	(28.8)	(5.7)	Doubtful hazard	
		53.0	(64.5)	(28.2)	(7.3)	Doubtful hazard	
½ $NaClO_3$ ½ As_2O_3	20	11.5	(80.8)	(17.2)	(2.0)	No hazard	(No precipitate in these mixtures)
		29.0	(78.6)	(17.2)	(4.2)	No hazard	
		43.0	(76.9)	(17.3)	(5.8)	No hazard	
½ $NaClO_3$ ½ As_2O_3	30	11.5	(71.8)	(26.4)	(1.8)	Hazard	
		29.0	(70.8)	(25.4)	(3.8)	Hazard	
		43.0	(70.5)	(24.6)	(4.9)	Hazard	
		53.0	(70.6)	(23.2)	(6.2)	Hazard	
½ $NaClO_3$ ½ Na_2HAsO_3	20	11.5	82.2	15.4	2.4	Hazard	
		29.0	79.8	14.9	5.3	Doubtful hazard	
		43.0	78.6	14.3	7.1	Doubtful hazard	
½ $NaClO_3$ ½ Na_2HAsO_3	30	11.5	75.4	22.4	2.2	Hazard	
		29.0	73.1	22.0	4.9	Hazard	
		43.0	71.5	22.2	6.3	Hazard	
½ $NaClO_3$ ½ Na_2HAsO_4	40	29.0	65.7	30.2	4.1	Hazard	
		43.0	62.6	27.3	10.1	Doubtful hazard	
½ $NaClO_3$ ½ Na_2HAsO_4	30	11.5	72.3	25.8	1.9	Hazard	
		29.0	70.6	24.5	4.9	Hazard	
½ $NaClO_3$ ½ NH_4CNS	30	11.5	71.0	27.5	1.5	Hazard	Solution clear at first but a heavy precipitate came out on standing. Slight odor of Cl_2
		29.0	69.3	27.2	3.5	Hazard	
		43.0	69.7	25.4	4.9	Hazard	

Experiments with Hydrated Chlorates

The experiments of the previous section show that any of the salts tested would have to be added to sodium chlorate in large proportions in order to reduce significantly the fire hazard accompanying the use of this substance. Furthermore, the salts most effective in reducing the combustibility are relatively non-toxic to plants and their addition to sodium chlorate will reduce the herbicidal power to a degree roughly proportional to the reduction in chlorate content. This consideration led to studies on another possible method of reducing the fire risk, namely, the application of the toxic chlorate ion in the form of one of its hydrated salts, such as barium or calcium chlorate.

Calcium chlorate carries two molecules of water of hydration, equivalent to 14.8% of the weight of the hydrated salt, and contains 68.8% chlorate ion calculated on the same basis. In comparison sodium chlorate carries no water of hydration, and is 78.4% chlorate. The herbicidal power of calcium chlorate, based on percentage chlorate, should therefore be somewhat lower than that of sodium chlorate.

Combustibility tests were made on cloth treated in 10, 20 and 30% solutions of calcium chlorate. The data obtained are presented in Table X. They show that material treated with 10% calcium chlorate becomes a doubtful hazard at a relative humidity of 43%, and is not completely safe until the humidity is raised to 61%. Material treated with 20% and 30% solutions of calcium chlorate become a doubtful hazard at 53% relative humidity, and the combustibility is not significantly changed by raising the humidity to

TABLE X

COMBUSTIBILITY OF $Ca(ClO_3)_2$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Results of combustion test
			Combustible material, %	Salt, %	Water, %	
$Ca(ClO_3)_2$	30	11.5	70.4	25.2	4.4	Hazard
		29.0	64.5	25.0	10.5	Hazard
		43.0	62.8	24.0	13.2	Hazard
		53.0	59.7	21.8	18.5	Doubtful hazard
		61.0	58.2	21.4	20.4	Doubtful hazard
$Ca(ClO_3)_2$	20	11.5	75.5	20.4	4.1	Hazard
		29.0	73.9	18.1	8.0	Hazard
		43.0	72.7	17.3	10.0	Hazard
		53.0	70.6	16.7	12.7	Doubtful hazard
		61.0	68.5	16.2	15.3	Doubtful hazard
$Ca(ClO_3)_2$	10	11.5	84.4	12.2	3.4	Hazard
		29.0	82.2	11.7	6.1	Hazard
		43.0	80.7	11.5	7.8	Doubtful hazard
		53.0	78.9	11.4	9.7	Doubtful hazard
		61.0	77.5	11.0	11.5	No hazard

61%. As material treated with sodium chlorate solutions is a definite fire hazard at all relative humidities below 75%, it is evident that calcium chlorate is the safer chemical for general use. The observed difference in inflammability between these two salts must be attributed to the water content of the calcium salt rather than to the lower percentage of chlorate, since

TABLE XI

COMBUSTIBILITY OF $Ba(ClO_3)_2$-CLOTH, $Ba(ClO_3)_2$-$CaCl_2$-CLOTH, AND $Ba(ClO_3)_2$-$MgCl_2$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Result of combustion test
			Combustible material, %	Salt, %	Water, %	
$Ba(ClO_3)_2$	30	11.5	71.3	26.8	1.9	Hazard
		29.0	70.0	26.2	3.8	Hazard
		43.0	69.6	26.0	4.4	Hazard
		53.0	68.5	25.4	6.1	Hazard
$Ba(ClO_3)_2$	20	11.5	79.0	18.9	2.1	Hazard
		29.0	77.2	18.8	4.0	Hazard
		43.0	76.2	18.9	4.9	Doubtful hazard
		53.0	75.8	18.0	6.2	Doubtful hazard
		61.0	75.1	17.8	7.1	Doubtful hazard
$Ba(ClO_3)_2$	10	11.5	85.9	12.2	1.9	Hazard
		29.0	84.4	11.6	4.0	Doubtful hazard
		43.0	83.5	11.7	4.8	Doubtful hazard
		53.0	82.4	11.5	6.1	No hazard
½ $Ba(ClO_3)_2$ ½ $CaCl_2$	40*	11.5	63.3	31.8	4.9	No hazard
		29.0	58.3	28.5	13.2	No hazard
		43.0	55.8	28.1	16.1	No hazard
½ $Ba(ClO_3)_2$ ½ $CaCl_2$	20	11.5	75.5	20.2	4.3	Doubtful hazard
		29.0	71.8	18.9	9.3	No hazard
		43.0	69.0	19.2	11.8	No hazard
½ $Ba(ClO_3)_2$ ½ $CaCl_2$	30	11.5	68.6	27.5	3.9	Doubtful hazard
		29.0	65.0	25.2	9.8	No hazard
		43.0	63.4	26.1	10.5	No hazard
½ $Ba(ClO_3)_2$ ½ $CaCl_2$	15	11.5	78.4	15.4	6.2	Doubtful hazard
		29.0	77.5	16.3	6.2	Doubtful hazard
		43.0	76.0	15.1	8.9	Doubtful hazard
½ $Ba(ClO_3)_2$ ½ $CaCl_2$	25	11.5	72.2	24.6	3.2	Doubtful hazard
		29.0	69.3	24.9	5.8	Doubtful hazard
		43.0	69.0	23.0	8.0	Doubtful hazard
½ $Ba(ClO_3)_2$ ½ $MgCl_2$	15	11.5	80.6	15.8	3.6	Doubtful hazard
		29.0	79.1	15.2	5.7	Doubtful hazard
		43.0	76.8	15.4	7.8	No hazard
½ $Ba(ClO_3)_2$ ½ $MgCl_2$	25	11.5	72.6	24.2	3.2	Doubtful hazard
		29.0	70.5	23.8	5.7	Doubtful hazard
		43.0	69.7	22.7	7.6	Doubtful hazard

**Slight precipitation.*

material treated in 20% and 30% solutions of calcium chlorate are less hazardous than material treated in 10% and 20% solutions of sodium chlorate respectively. The contribution of the water carried by the hydrated salt to the total water content of the test pieces is indicated in the sixth column of Table X by the different percentages of water corresponding to the different concentrations of test solution. The fact remains, however, that calcium chlorate is quite dangerous at all ordinary atmospheric humidities. As calcium chlorate is difficult to prepare, and would probably prove too expensive for use as a herbicide, no further studies were made on this salt.

Barium chlorate contains only one molecule of water of hydration, equal to 5.6% of the weight of the hydrate. The percentage of chlorate ion in this compound is 51.8. Combustibility tests were conducted on cloth treated with 10, 20 and 30% solutions of this salt, and the results obtained are presented in Table XI. The data show that material treated with barium chlorate is less combustible than material treated with sodium chlorate, but in spite of its lower chlorate content, barium chlorate renders organic material more combustible than calcium chlorate. The lower hydration of this salt compared with calcium chlorate is also evident from a comparison of column 6, Tables X and XI. Barium chlorate would therefore be rather dangerous to use alone as a herbicide.

The feasibility of adding other salts to barium chlorate in order to reduce the fire risk was next investigated. Calcium and magnesium chlorides were used as these were found, in the previous experiments, to be most effective in reducing the fire risk involved in the use of sodium chlorate as a herbicide. Various proportions of these salts were tested and the results obtained are given in Table XI. The reduced combustibility and increased moisture content of material treated with these mixed herbicides in comparison with those treated with pure barium chlorate solutions is evident from the data. Herbicide mixtures composed of two-thirds barium chlorate and one-third of either anhydrous calcium or magnesium chloride will be entirely safe at ordinary atmospheric humidities.

Experiments with Sodium Dichromate

Sodium dichromate forms a major part of at least one commercial herbicide and preliminary tests (2) of its toxicity to plants suggest that it may have valuable herbicidal properties. As it is also a strong oxidizing agent, some tests were conducted to determine to what extent its use was accompanied by fire risk. Sodium dichromate-organic matter mixtures should be less hazardous than chlorate-organic matter mixtures since this dichromate salt carries two molecules of water of crystallization and has a greater equivalent weight.

The technique employed in these tests was the same as that previously described. The cloth test pieces were treated in sodium dichromate solutions of 10, 20, 30, 40 and 50% concentrations, and filter paper was treated in

solutions of 10, 30 and 50% concentrations. The amount of sodium dichromate taken up from these solutions by the two test materials is shown in Fig. 4 A. This shows again a linear relation similar to that obtained with sodium chlorate solutions (Fig. 3 A).

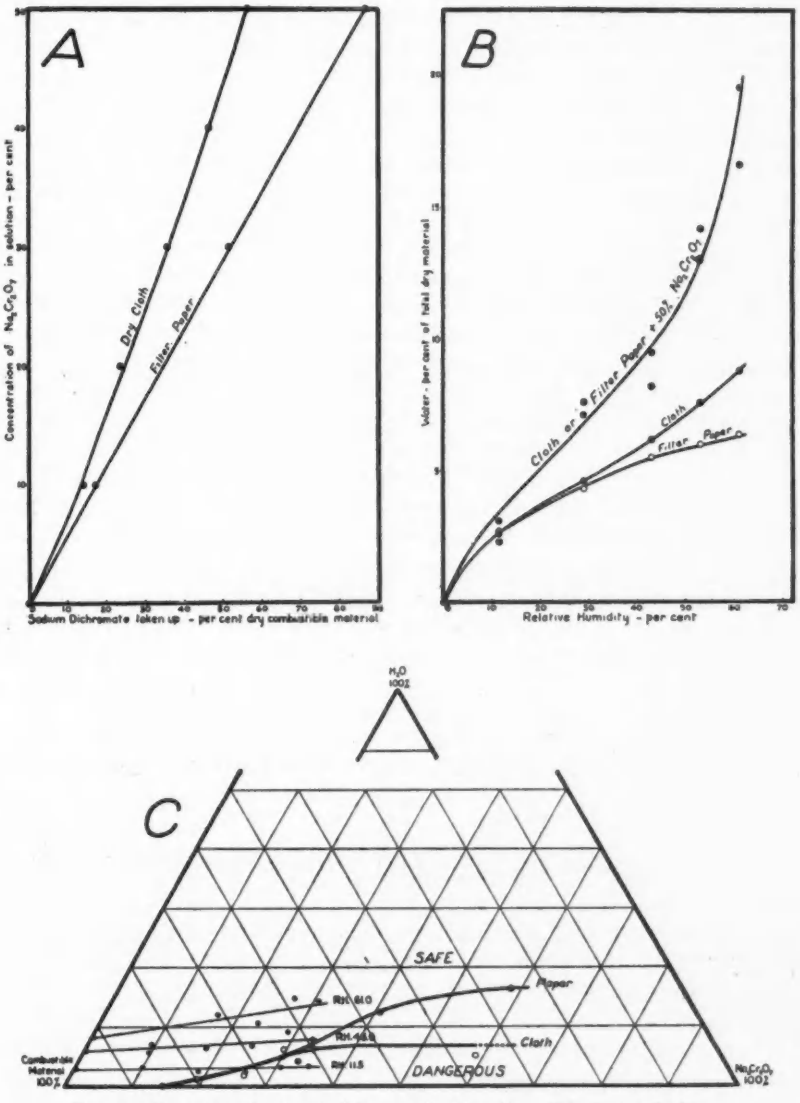


FIG. 4. *Properties of test materials treated with sodium dichromate solutions.*

The amount of moisture taken up by untreated cloth and filter paper, and by the same material treated with a 50% solution of sodium dichromate is shown in Fig. 4 B. As the dichromate salt takes up two molecules of water of crystallization, the treated materials took up more moisture than the untreated. This is the opposite behavior from that of test pieces treated with sodium chlorate which, at vapor pressures less than that of a saturated solution, took up less moisture than untreated material. (Fig. 3 B).

A saturated solution of sodium dichromate was found, in these experiments, to have a vapor pressure equivalent to a relative humidity of 53% at 25° C. Organic material containing sodium dichromate will therefore take up sufficient moisture to dissolve the salt when the humidity is above 53%. In these experiments the test pieces were conditioned, in succession, at relative humidities of 0, 11.5, 29, 43, 53 and 61%. The composition of the test pieces conditioned at 11.5, 43, and 61% relative humidity is shown in Fig. 4 C, the construction of which is similar to that of Fig. 3 C. The values at 61% relative humidity are not considered very reliable as some of the saturated solution may have drained off the material before weighing.

On determining the combustibility of the test materials treated with sodium dichromate, it was found that pieces soaked in 10 and 20% solutions were not hazardous even at relative humidities as low as 11.5%. None of the test materials, including filter paper soaked in a 50% solution, could be considered hazardous at a relative humidity of 43%. The complete results are shown in the triangular diagram, Fig. 4 C. The data shown on this chart were obtained in the same manner as those described under the tests on sodium chlorate, a few test pieces being soaked in saturated sodium dichromate in order to extend the range of the curves.

Comparison of Fig. 4 C with Fig. 3 C shows that sodium dichromate-organic matter mixtures are not nearly as combustible as similar mixtures

TABLE XII

COMBUSTIBILITY OF $Na_2Cr_2O_7$-$CaCl_2$-CLOTH, AND $NaClO_3$-$Na_2Cr_2O_7$-CLOTH MIXTURES

Composition of salt mixture	Concentration of test solution, %	Relative humidity used for conditioning, %	Composition of test material			Results of combustion test
			Combustible material, %	Salt, %	Water, %	
½ $Na_2Cr_2O_7$ } ½ $CaCl_2$ }	60	11.5	56.9	40.9	2.2	Doubtful hazard
		29.0	55.1	38.7	6.2	No hazard
½ $NaClO_3$ } ½ $Na_2Cr_2O_7$ }	40	11.5	64.8	32.8	2.4	Hazard
		29.0	61.2	33.1	5.7	Hazard
		43.0	61.5	32.6	5.9	Hazard
½ $NaClO_3$ } ½ $Na_2Cr_2O_7$ }	30	11.5	70.4	27.4	2.2	Hazard
		29.0	70.1	25.6	4.3	Hazard
		43.0	70.0	23.8	6.2	Hazard

with sodium chlorate. Admixture of small quantities of the dichromate salt with organic material does not affect the combustibility of the material appreciably, whereas a small amount of chlorate renders it hazardous.

The results show that, even under dry conditions, organic material contaminated with sodium dichromate can scarcely be considered dangerous. Mixtures containing high percentages of dichromate, however, may be somewhat dangerous. In order to ensure safety under all conditions, tests were made on mixtures composed of five-sixths sodium dichromate and one-sixth anhydrous calcium chloride. The results obtained for a 60% solution of this mixture are presented in Table XII. This mixture was found to be safe at a relative humidity of 29%, showing that when a small amount of calcium chloride is added to sodium dichromate this material is entirely safe.

Mixtures of sodium dichromate and sodium chlorate have been used as commercial herbicides, and although these may be effective from the standpoint of weed eradication, there is no reason to believe that the small amount of water held by the sodium dichromate will cause any significant reduction in the fire risk. Mixtures composed of equal parts of sodium dichromate and sodium chlorate, and two-thirds sodium dichromate and one-third sodium chlorate, were tested and the results are also given in Table XII. Both of these mixtures were, if anything, more hazardous than similar concentrations of pure sodium chlorate at relative humidities up to 43%, the highest value tested. Herbicides of this composition are therefore extremely dangerous.

Experiments with Potassium Permanganate

The effect of potassium permanganate, another oxidizing agent, on the combustibility of organic material was tested, although this chemical is not commonly used as a herbicide, and appears to be useless for this purpose (2). Test pieces of cloth and filter paper were soaked in an aqueous solution of potassium permanganate, saturated at 25° C. (7.6%). These pieces darkened considerably on drying but when conditioned at a relative humidity of 29% they were no more combustible than the untreated material. Apparently potassium permanganate is not hazardous, although it oxidizes the organic matter to some extent at room temperature.

Relative Humidity in Relation to Fire Risk

A survey of the results obtained shows that the fire risk involved in the use of a chlorate-containing herbicide will depend largely on the relative humidity to which material, contaminated with the herbicide, is exposed. To obtain some information on the relative humidity of the atmosphere, official records (4) were consulted.

The important point from the standpoint of this investigation was to determine how frequently the humidity fell below certain minimal values. This was done by obtaining the number of days on which the humidity fell below 30 and 40% at five western and one eastern station during the months

of June, July and August, for the five-year period 1924 to 1928 inclusive. At most of these stations the observations were made in the morning and evening only, when the temperature was usually lower than the maximum for the day, and consequently give humidity readings higher than the minimum values for most days. By assuming that the total water content of the air was the same at the hottest period of the day as it was when the humidity was measured it was possible to calculate the minimum relative humidity for any day. When this correction was applied to the data from the western stations it was found almost to double the number of days the humidity fell below 30%.

The summarized data are presented in Table XIII. This table is divided into three sections. The first section shows the number of days during the

TABLE XIII

NUMBER OF DAYS ON WHICH THE RELATIVE HUMIDITY FELL TO 30 AND 40%, OR LOWER, DURING JUNE, JULY AND AUGUST AT SELECTED STATIONS. DATA FOR YEARS 1924 TO 1928 INCLUSIVE

Year	Edmonton	Medicine Hat	Moose Jaw	Saskatoon	Winnipeg*	Ottawa
Number of days on which the observed humidity fell to 30% or lower						
1924	11	21	2	1	4	0
1925	14	26	6	0	1	0
1926	6	21	7	0	3	0
1927	3	4	1†	0	12‡	0
1928	0	5	0	0†	0	0
Number of days on which the humidity probably fell to 30% or lower during hot part of day						
1924	19	36	3	11	Observations,	0
1925	20	40	17	7	as given	0
1926	10	27	11	16	above,	0
1927	4	7	7†	1	were taken	0
1928	0	7	0	1†	at 2 p.m. Hence no calculations made.	0
Number of days on which the observed humidity fell to 40% or lower						
1924	30	45	10	5	21	0
1925	34	49	31	1	15	0
1926	29	47	20	2	28	0
1927	18	21	11†	0	21‡	0
1928	10	19	0	0†	1	0

Observations at Winnipeg taken at 2 p.m. At all other stations observations were taken in the evening, 5.45 p.m. to 8.00 p.m., exact time varying with station and year.

†*Observations for two months only.*

‡*Observations for one month only.*

three-month period on which the observed humidity was below 30%; the second section shows the number of days on which the humidity was probably 30%, or lower, during the hot part of the day; the final section shows the number of days on which the observed humidity fell below 40%. The number of days on which the relative humidity fell below 40% during the period of maximum temperature was not calculated, but this does not affect the conclusions to be drawn, since the figures show that even the observed humidity is frequently below 40%.

The results show that low relative humidities are quite frequent in the drier regions of western Canada. Thus at Medicine Hat in 1925 there were 26 days on which the observed humidity fell to 30% or lower, 40 days on which the humidity was probably below 30% during the hot part of the day, and 49 days on which the observed humidity fell to 40% or lower. Low relative humidities are less frequent at the other western stations, but it is the extreme conditions that must be taken into account. In contrast to the above, the observed relative humidity at Ottawa never fell below 40%.

It is unlikely that the relative humidity remains below these low values for more than a few hours, and it is only during this period that a herbicide containing chlorate and sufficient water-absorbing chemical for protection at higher humidities will involve a fire risk. It was found in this investigation that most of the treated test material dried rather slowly when exposed to atmospheres of lower relative humidity, but gained weight quite rapidly when placed in atmospheres of higher relative humidity. Slow drying was in particular evidence when the moisture-retaining salt passed through a transition point. These observations support the contention that the period of danger may be of shorter duration than the period of low humidity. On the other hand it must be remembered that the humidity will normally decrease gradually, and it is possible that the herbicide will remain in practical equilibrium with it. In the interests of safety, therefore, it seems best to regard the herbicide as dangerous during the entire period that the humidity is below a certain value dependent on the kind and amount of the water-absorbing chemical present in the mixture.

As the relative humidity at western points frequently falls below 40%, it is evident that any chlorate herbicide in general use must contain sufficient protecting chemical to render it entirely safe at this relative humidity. To produce a chlorate herbicide that would be safe at relative humidities of 30% or less, would require a large proportion of protecting chemical and would doubtless prove to be impracticable owing to the cost and loss of herbicidal power. Considering this question of practicability, and bearing in mind the probability that this low relative humidity seldom occurs for more than short periods even in the drier districts, it would appear justifiable to employ a herbicide that, although not entirely free from risk, would be no more than a doubtful hazard under these conditions.

Conclusions

Accepting as safe herbicides only those that are not hazardous at 40% relative humidity, and no more than a doubtful hazard at 30% relative humidity, regardless of the proportions of herbicide and combustible material, only a few of the numerous mixtures tested come within this category. These are:* (1) one-half sodium chlorate plus one-half calcium chloride; (2) two-thirds sodium chlorate plus one-third magnesium chloride; (3) one-half sodium chlorate plus one-half sodium hydroxide; (4) two-thirds barium chlorate plus one-third calcium chloride; (5) two-thirds barium chlorate plus one-third magnesium chloride; (6) five-sixths sodium dichromate plus one-sixth calcium chloride; and (7) five-sixths sodium dichromate plus one-sixth magnesium chloride.

Comparing the first two mixtures listed, it seems probable that the superior protecting action of magnesium chloride over calcium chloride is exaggerated by these proportions. Calcium chloride does not provide the required protection when it forms only one-third of the mixture, as does magnesium chloride, but it would probably have been effective at some proportion between one-third and one-half of the mixture, had such a proportion been tested.

The value of chlorate-sodium hydroxide mixtures is somewhat doubtful. According to these tests this mixture is not hazardous, but exposure to air would convert much of the hydroxide to carbonate. Mixtures composed of one-half sodium chlorate plus one-half sodium carbonate were found to be hazardous, and although a mixture composed of one-half sodium hydroxide originally would correspond to a somewhat higher proportion of carbonate, it is doubtful, judging from the data in Table V, if such a mixture would meet the above requirements for a safe herbicide.

Barium chlorate has to be mixed with only one-half its weight of either anhydrous calcium chloride or magnesium chloride to be safe. Since calcium chlorate alone is less hazardous than barium chlorate alone it seems likely that these proportions of calcium and magnesium chlorides would also remove any fire risk involved in the use of calcium chlorate. Sodium dichromate is comparatively non-hazardous and is rendered entirely safe when either calcium or magnesium chloride forms one-sixth of the mixture.

The herbicidal power of these mixtures must be taken into account in considering which ones would be most valuable in practice. Sodium dichromate appears to be more toxic than sodium chlorate, when tested on annual weeds in a greenhouse (2), but the results of field experiments (10) indicate that it is less effective than sodium chlorate for eradicating perennials. Herbicides based on sodium dichromate are therefore of uncertain value at the present time.

Greenhouse tests of toxicity to annuals (2) indicate that sodium chlorate is more toxic than barium chlorate. This might be expected, since the per-

*Proportions of all chemicals are on an anhydrous basis.

centage of chlorate ion in sodium chlorate is higher than in barium chlorate. Some idea of the relative herbicidal power of the "safe" chlorate herbicides listed above can be obtained from the percentage of chlorate ion they contain. This information is shown in Table XIV, the chlorate being expressed as a percentage of the hydrated material, since this is the form that will be used in practice. The composition of sodium chlorate is also shown for comparison.

TABLE XIV

CHLORATE CONTENT OF "SAFE" HERBICIDES

Composition of mixture on anhydrous basis	Chlorate in final hydrated mixture, %
$\frac{1}{2}$ $NaClO_3$ + $\frac{1}{2}$ $CaCl_2$	26.3
$\frac{1}{2}$ $NaClO_3$ + $\frac{1}{2}$ $MgCl_2$	37.9
$\frac{2}{3}$ $Ba(ClO_3)_2$ + $\frac{1}{3}$ $CaCl_2$	26.8
$\frac{2}{3}$ $Ba(ClO_3)_2$ + $\frac{1}{3}$ $MgCl_2$	25.8
$NaClO_3$	78.4

Judging from the chlorate content alone the mixture composed of two-thirds sodium chlorate and one-third magnesium chloride would be the most effective of the safe herbicides. However, it would only be about one-half as toxic as pure sodium chlorate. The other three mixtures have about the same chlorate content and would only be about one-third as toxic as sodium chlorate. These deductions do not take the herbicidal power of the water-absorbing chemical into account. Preliminary tests (2) indicate that the minimum lethal dose of calcium chloride is about twice that of sodium chlorate. If magnesium chloride has about the same toxicity it is doubtful if these added chemicals contribute much to the killing power of the herbicide.

Acknowledgment

The author wishes to thank Mr. R. C. Rose, Research Assistant, University of Alberta, for technical assistance during the course of this investigation.

Addendum

Since the submission of this paper for publication Tingey (13) has reported spontaneous combustion of weeds on plots sprayed two hours previously with Atlacide. Thermohygrograph records show that, about the time combustion took place, the atmospheric temperature rose sharply from 65 to 75° F. and the relative humidity fell from 66 to 31%. Atlacide, however, is not calcium chlorate as stated by Tingey, but a mixture of approximately two-thirds sodium chlorate and one-third calcium chloride. The results presented in Table III of the present paper show that organic matter mixed with material having the composition of Atlacide is somewhat dangerous at relative humidities below 53%, and will become a distinct fire hazard at the low humidity reported by Tingey. Atlacide should not be confused with pure calcium chlorate; the results shown in Table X of the present paper were obtained with the latter chemical.

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STUDIES ON FOOT AND ROOT ROT OF WHEAT

II. CULTURAL RELATIONSHIPS ON SOLID MEDIA OF CERTAIN MICRO-ORGANISMS IN ASSOCIATION WITH *Ophiobolus graminis* SACC.[1]

By W. C. Broadfoot[2]

Abstract

The antagonistic and compatible growth relationships of 66 cultures of bacteria and fungi, most of which were from the soil, towards *O. graminis* on potato dextrose agar and Molisch's salt peptone agar, were compared with the effect of each on the virulence of this pathogene on wheat seedlings in open soil culture.

Of the 21 cultures which controlled the virulence of *O. graminis* in the soil, only 15 of these were antagonistic on potato dextrose agar, while of the 45 cultures which gave intermediate or no control, 17 were compatible and 28 were decidedly antagonistic. From data secured indirectly, the antagonism or compatibility of the micro-organisms toward *O. graminis*, observed on potato dextrose agar, did not seem to depend on active alkali or acid more than on other metabolic products. The study apparently demonstrates that the growth reaction of various micro-organisms and *O. graminis*, associated on the two solid media used, is not a reliable indication that the same micro-organism will or will not suppress the virulence of this pathogene on wheat in soil in open pot culture.

Ever since pure-culture methods have been perfected, the usual procedure in investigations has been with one organism kept pure and free from contamination. However, in nature, and especially in the case of soil-borne diseases, it would seem that more than one micro-organism is frequently associated in the host-parasite relationship.

Porter (15), Machacek (13), and later Fawcett (10) have emphasized the association effects of other micro-organisms in the production and symptoms of certain diseases in plant tissue. Savastano and Fawcett (20), Vasudeva (23, 24), Bamberg (1), Sanford and Broadfoot (18), Henry (11, 12), Moritz (14), Endo (8, 9), Broadfoot (2), and others have dealt with cases in which certain other fungi and bacteria modified the virulence of plant diseases. Dickson (6), Vanterpool (22), Valleau and Johnson (21), and others have demonstrated that the symptoms characteristic of a single virus may be altered by mixing certain plant viruses. Fawcett (10) mentions two general types of investigations in this connection; *viz.*, (1) the study in a quantitative as well as qualitative way of the effect of known mixtures or combinations of micro-organisms in culture media, and (2) the study in the same way of the effect on development of diseases by inoculation of plants with known mixtures of micro-organisms.

[1] *Manuscript received March 29, 1933.*

Contribution from the Division of Botany, Experimental Farms Branch, Department of Agriculture, Canada, co-operating with the University of Alberta. This paper constitutes one part of a thesis submitted May 3, 1932, to the graduate faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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In the work of Sanford and Broadfoot (18), which deals with the second type of investigation, the virulence of *Ophiobolus graminis* on wheat plants was profoundly modified, and at times controlled, by the association of cultures or filtrates of a number of soil-inhabiting bacteria and fungi. In producing this condition, there did not appear to be any difference whether fungi or bacteria, as classes, were concerned, but rather it was a case of the kind of organism or organisms which were associated. That the suppressive effect was probably due, directly or indirectly, to toxicity or staling products of the living cultures, or of their filtrates, and not to competition or to the hydrogen ion reaction was strongly suggested.

As a result of these conclusions it was decided to culture each of the micro-organisms, used in the original experiment mentioned, with *O. graminis* on a solid substrate, to see if the growth effects would be the same as in the soil. Should there be uniformity in this regard, a convenient and rapid method would be available for observing the probable antagonism or compatibility of such associations in the soil.

Material and Methods

The suitability of the following media for culturing *O. graminis* was tested: Dox's inorganic salt; Brown's synthetic; Czapek's; Harvey's glucose-glycerol; Molisch's salt peptone; Peptone sucrose; Waksman's sucrose peptone; Bezancon's glycerol peptone; Zike's magnesium sucrose asparagin; Woltze's sucrose ammonium sulphate; Heinemann's asparagin; Bokorny's ethyl alcohol ammonium sulphate; and potato dextrose. As *O. graminis* grew best on Molisch's salt peptone agar and on potato dextrose agar, these were employed.

A uniform portion of inoculum of *O. graminis* was planted on potato dextrose agar approximately 30 mm. from the edge of the Petri plates, and allowed to grow for three days, then the other organism was placed about 30 mm. from the growing colony of *O. graminis*. Separate tests were made of each of the micro-organisms studied. Each test was in triplicate. The general experiment was repeated four times. The first and second times, the cultures were grown on 15 cc. of potato dextrose agar, but the third and fourth times, on 25 cc. of potato dextrose agar and Molisch's salt peptone agar, respectively, contained in 250-cc. Erlenmeyer flasks. The initial pH reaction of the potato dextrose agar was 6.7, and that of Molisch's salt peptone 5.7. Notes were taken on the degree of antagonism or compatibility between *O. graminis* and the various introduced micro-organisms after the cultures had incubated 18 days.

Preliminary study in 1930 suggested that the growth reaction could be divided for the purpose intended into two main types, *viz.*, antagonistic and compatible. The former type is indicated by definite antagonism between the cultures, and compatibility by an intermingling or growing together of the two organisms. A subdivision of each general type was made as follows:

I. Antagonistic

A. A distinct neutral zone between *O. graminis* and the introduced organism.

B. A distinct line of demarcation between *O. graminis* and the introduced organism.

II. Compatible

A. *O. graminis* grows over introduced organism.

B. Introduced organism grows over *O. graminis*.

The two classes, indicating the two degrees of antagonism, are illustrated in Fig. 1, I (A) and I (B), respectively. The non-antagonistic or compatible types of growth are illustrated in Fig. 1, II (A) and II (B), respectively.

Zeller and Schmitz (26), Cook (4), Porter (16, 17), Brown (3), Machacek (13), Endo (7) and others have studied the association of phytopathogenes in culture. Endo (7) of Japan, classifying in plate culture the growth reaction between *Hypochnus centrifugus* and other micro-organisms, apparently used a similar scheme to that employed in this study, except that an extra type (class I (B)) has been described here. Two of his classes appear to be the same as ours, *i.e.*, I (A) and II (B). Endo describes Class II (B), where the introduced organism grows over the other, as antagonistic; but we feel that it should be classed as compatible, since both organisms intermingle. Apparently he did not recognize, or at least describe, a type corresponding to Class I (B), where there is a sharp line of demarcation between the two organisms. His Fig. 2, in Plate III, illustrating the growth relation between *H. centrifugus* and *Bacillus cereus*, suggests the presence of a type of reaction similar to class I (B) used here.

Experimental Results

Association Effects on Solid Media

The growth reaction of each of 66 fungi and bacteria when associated with *O. graminis* on potato dextrose agar and on Molisch's salt peptone agar is given in Table I, according to the types indicated under methods. There was, except for minor variations, fairly good agreement in the results obtained in the three tests made on potato dextrose agar. In the case of Molisch's salt peptone agar, the growth reaction was frequently different from that on potato dextrose agar. This would be expected, since the same organism with its complement of enzymes might produce different end-products of metabolism on media of different composition. For example, 38 of the 66 micro-organisms mentioned above were antagonistic to *O. graminis* on both media, while nine of them were compatible. On the other hand, cultures Nos. 16, 23, and 49 were compatible on Molisch's salt peptone agar and antagonistic to *O. graminis* on potato dextrose agar. Again, cultures Nos. 18, 33, 38, 44, 48, 51, 61, and 63 were antagonistic on the former and compatible on the latter substrate.

TABLE I

THE GROWTH REACTION OF 66 CULTURES OF FUNGI AND BACTERIA IN ASSOCIATION WITH *Ophiobolus graminis* SACC. ON TWO NUTRIENT AGARS[a], AND THE EFFECT OF EACH CULTURE ON THE VIRULENCE OF THE PATHOGENE ON WHEAT SEEDLINGS IN SOIL CULTURE, AND ALSO THE pH VALUES OF THE POTATO DEXTROSE CULTURE DECOCTION

Culture	Potato dext. Growth type[b]				Molisch's pept. Growth type				pH Pot. dext. cult. decoc'n[c]	Effect on virulence of pathogene[d]
	I		II		I		II			
	A	B	A	B	A	B	A	B		
1. *Helminthosporium sativum*		X				X		X	6.7	NC
2. *Fusarium culmorum*				X				X	5.6	NC
3. *Wojnowicia graminis*		X			X				6.6	C
4. *Leptosphaeria herpotrichoides*		X				X			6.1	IC
5. *Sclerotinia* sp.	X					X			5.0	NC
6. *Fusarium culmorum*				X				X	6.0	IC
7. *Ascochyta graminicola*		X			X				6.7	NC
8. Bacteria	X				X				7.3	NC
9. Fungus				X				X	6.8	NC
10. *Plenodomus meliloti*		X			X				6.2	C
11. *Helminthosporium sativum*		X				X			7.0	C?
12. *Rhizoctonia* sp.				X				X	6.7	NC
13. *Actinomyces* sp.	X				X				6.3	IC
14. *Bacterium transluscens undulosum*	X					X			8.4	C
16. Fungus		X					X		6.0	IC
17. Fungus		X				X			5.3	IC
18. *Typhula graminum*			X			X			6.7	IC
19. Bacteria	X				X				7.2	C
20. Bacteria	X				X				7.3	C
21. Bacteria	X				X				5.7	NC?
22. Bacteria	X				X				4.3	C
23. *Plenodomus destruens*		X					X		6.3	NC
24. *Plenodomus chelidanii*		X				X			6.4	C
25. Fungus		X			X				7.0	NC
26. Fungus				X				X	6.4	C
27. Fungus		X			X				5.3	NC
28. *Actinomyces* sp.		X			X				7.3	NC
29. Bacteria	X					X			5.6	IC
30. Bacteria	X				X				7.2	C
31. Bacteria		X							5.8	NC
32. *Actinomyces* sp.		X			X				5.8	NC
33. Bacteria			X		X				5.2	NC
34. Bacteria	X								7.5	NC
35. Bacteria			X						7.3	IC
36. Bacteria	X				X				7.0	C
37. Bacteria	X				X				5.9	IC
38. Bacteria			X			X			6.3	C
39. Bacteria			X						6.5	IC
40. Bacteria			X						7.1	IC
41. Bacteria	X				X				7.1	C
42. Bacteria			X						7.1	C
43. Bacteria	X				X				7.6	C
44. Bacteria			X		X				6.8	NC
45. Bacteria		X			X				7.0	IC

[a] *Potato dextrose agar and Molisch's salt peptone agar.*

[b] *Types I, antagonistic; II, compatible; see context for description of subtypes A and B.*

[c] *pH values of potato dextrose culture decoction; and* [d] *effect on virulence of O. graminis (C, control; IC, intermediate control; NC, no control), data of both taken from Table II of context reference (18).*

PLATE I

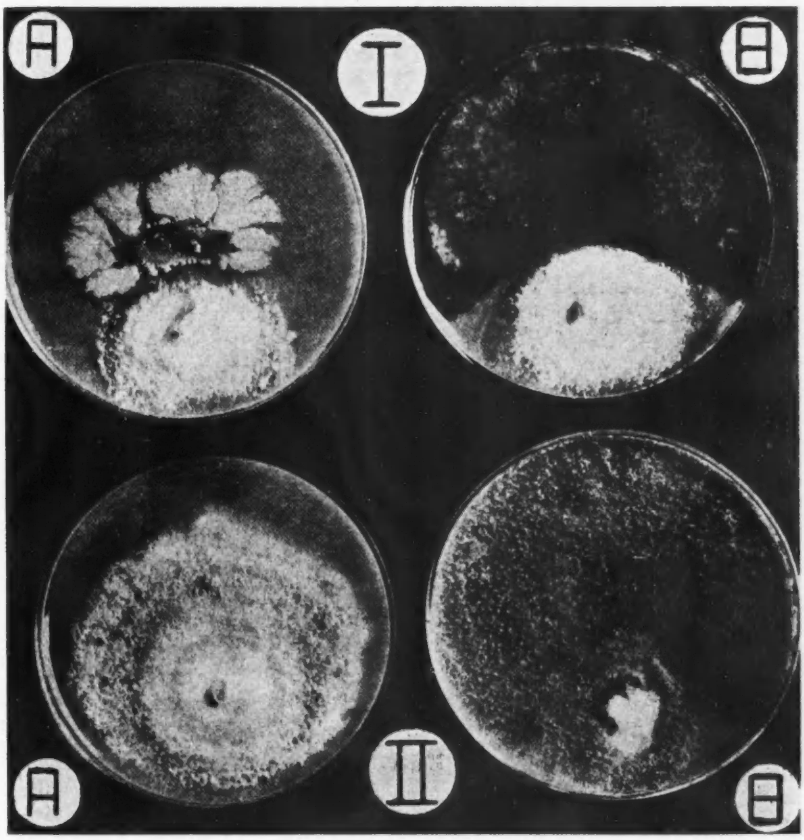

FIG. 1. *Examples of antagonism and compatibility between Ophiobolus graminis Sacc. and other micro-organisms on potato dextrose agar. I. Antagonism. Subtype (A), a distinct neutral zone between O. graminis and culture No. 20. Subtype (B), a sharp line of demarcation between O. graminis and culture No. 1. II. Compatibility. Subtype (A), O. graminis grows over culture No. 55. Subtype (B), culture No. 12 grows over O. graminis.*

TABLE I—*Concluded*

Culture	Potato dext.				Molisch's pept.				pH Pot. dext. cult. decoc'n[c]	Effect on virulence of pathogene[d]
	Growth type[b]				Growth type					
	I		II		I		II			
	A	B	A	B	A	B	A	B		
46. *Ophiobolus graminis*			X				X		6.5	NC
47. Bacteria	X				X				7.8	C
48. *Bacillus fecalis alcaligines*			X		X				8.8	NC?
49. *Botrytis cinerea*		X					X		3.8	C
50. *Bacillus coli*			X						7.0	C?
51. *Bacillus butyricum*			X		X				7.5	NC
52. *Bacillus cinnebareus*		X			X				7.6	IC?
53. *Bacillus cereus*			X				X		8.4	C?
54. *Bacterium anthracoides*	X				X				8.5	IC?
55. *Bacillus mycoides*			X				X		6.2	NC
56. *Bacillus megaterium*	X				X				6.7	NC
57. *Bacillus subtilis*			X				X		9.0	C?
58. *Bacillus vulgatus*	X				X				6.7	C
59. *Bacillus ramosus*	X					X			6.7	NC
60. Bacteria			X						6.7	NC
61. Bacteria			X		X				7.6	NC
62. *Penicillium* sp.		X				X			5.5	IC?
63. *Rhizopus* sp.				X		X			3.8	NC
64. Bacteria		X				X			6.7	NC
65. Bacteria	X				X				7.3	NC
66. Bacteria	X				X				8.8	NC
67. Bacteria	X				X				6.7	NC

Association Effects on Potato Dextrose Agar Compared with those in the Soil on the Virulence of O. graminis on Wheat Seedlings

Taken from the original paper of Sanford and Broadfoot (18) and also included in Table I for comparison, are the association effects of the same cultures on the virulence of *O. graminis* on Marquis wheat seedlings grown in soil. One might expect that each of the organisms that controlled in soil culture the virulence of *O. graminis* on wheat seedlings, would also be antagonistic when grown with it on potato dextrose agar. However, this does not appear to be the case. Forty-three of these micro-organisms were antagonistic, and 23 were compatible. Of the 21 which controlled the virulence of *O. graminis* in soil culture (Nos. 3, 10, 11, 14, 19, 20, 22, 24, 26, 30, 36, 38, 41, 42, 43, 47, 49, 50, 53, 57, and 58), fifteen of these (Nos. 3, 10, 11, 14, 19, 20, 22, 24, 30, 36, 41, 43, 47, 49, and 58) were antagonistic, whereas six (Nos. 26, 38, 42, 50, 53, and 57) were not antagonistic.

On the other hand, it might be expected that the cultures which gave intermediate or no control of *O. graminis* in soil culture would not be antagonistic on potato dextrose agar. Of the 45 cultures which gave intermediate or no control of *O. graminis* in soil culture, 17 were not antagonistic, while 28 were decidedly antagonistic. The antagonistic cultures were Nos. 1, 4, 5, 7, 8, 13, 16, 17, 21, 23, 25, 27, 28, 29, 31, 32, 34, 37, 45, 52, 54, 56, 59, 62, 64, 65, 66, and 67.

Compatibility and Antagonism in Relation to Acids and Alkalies Produced in Culture

It was believed possible that the association effects observed on solid media might be influenced directly by acids or alkalies produced by the associated fungi. In the absence of information obtained directly from the solid media on which the micro-organism grew, it was decided to use, as a basis for comparison, the data published by Sanford and Broadfoot (18), which are listed in Table II. These values represent the final reaction of the potato dextrose decoction in which the various micro-organisms grew, and they should indicate the tendency of each culture to produce acids or alkalies on potato dextrose agar of essentially the same composition as the decoction.

Thus, in comparing the pH values of the decoction of the 66 cultures, and considering first the 43 cultures, which on the solid substrate were antagonistic to *O. graminis*, we find (Table II) that 11.6% of these had pH values between 3.8 and 5.4; 14.0% between 5.5 and 5.9; 58.1% between 6.0 and 7.4; 9.3% between 7.5 and 7.9; and the remaining 7.0%, values between 8.0 and 9.0. Of the 23 compatible cultures, 8.7% had values between 3.8 and 5.4; 4.3% between 5.5 and 5.9; 65.2% between 6.0 and 7.4; 8.7% between 7.5 and 7.9; and the remaining 13.0% of the cultures, values between 8.0 and 9.0. Apparently 58.1% of the antagonistic cultures, and 65.2% of the compatible cultures had pH values between 6.0 and 7.4, which range is, according to Davis (5), and Webb and Fellows (25), the optimum for good growth of *O. graminis* although depending somewhat on the strain concerned, as well as on the physical and chemical nature of the media.

Thus, on the basis of comparison used above, the antagonism or compatibility exhibited was, in many cases, not a direct result of active acidity or alkalinity, but rather due to other metabolic products of one or both associated micro-organisms, which conclusion agrees with that of Machacek (13).

TABLE II

THE ANTAGONISTIC OR COMPATIBLE GROWTH TYPES OF 66 MICRO-ORGANISMS IN ASSOCIATION WITH *Ophiobolus graminis* SACC. ON POTATO DEXTROSE AGAR ARRANGED ACCORDING TO THE pH VALUES OF THE POTATO DEXTROSE CULTURE DECOCTION IN WHICH THEY WERE ALSO CULTURED

Growth types	pH value classes*										Total no.
	3.8–5.4		5.5–5.9		6.0–7.4		7.5–7.9		8.0–9.0		
	No.	%	No.	%	No.	%	No.	%	No.	%	
Antagonistic	5	11.6	6	14.0	25	58.1	4	9.3	3	7.0	43
Compatible	2	8.7	1	4.3	15	65.2	2	8.7	3	13.0	23
	7	10.6	7	10.6	40	60.6	6	9.1	6	9.1	66

**Data taken from Table II, context reference (18).*

Discussion

Considering the results obtained from the foregoing studies, many of the micro-organisms which exercised a marked degree of control on the virulence of *O. graminis* on wheat seedlings in soil, in open pot culture, were not antagonistic to the pathogene on potato dextrose agar and on Molisch's salt peptone agar. In fact, more than one-half of the 66 cultures of fungi and bacteria employed in the study, which exhibited little or no effect on the virulence of *O. graminis* in soil, were decidedly antagonistic on potato dextrose agar. Likewise, many that controlled or greatly suppressed the virulence of this pathogene in soil were compatible on the media mentioned. Also many of the cultures which were compatible on potato dextrose agar were antagonistic on Molisch's salt peptone agar, and *vice versa*. A possible explanation for this, as it concerns both artificial media and the soil, is that the various micro-organisms, each with its complement of enzymes, produce substances which differ in kind and amount, according to the substrate.

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The writer is especially indebted to Dr. G. B. Sanford, Pathologist-in-charge, Dominion Laboratory of Plant Pathology, Edmonton, for suggestions and criticisms regarding these investigations, and to Dr. E. C. Stakman, Plant Pathologist, University of Minnesota, for his valuable criticisms.

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AN EXAMINATION OF IMMUNE SERUM LIPOIDS FOR THE COMPLEMENT FIXING ANTIBODIES OF TUBERCULOSIS[1]

By A. Hambleton[2]

Abstract

Lipoids which were extracted from immune tuberculosis serum at low temperatures by various procedures and solvents were examined by the tuberculo-complement-fixation test; antibodies were not found in the lipoid fractions, but were retained with the protein fraction of the serum. The use of desorbents, benzoic acid in alcohol, or saponin,—during the extraction, or the preliminary destruction of serum proteins by trypsin, did not result in antibodies being detected in the lipoid fractions. These results conform with other evidence which suggests that antibodies are protein in nature.

There exist at present no adequate data concerning the chemical and physical structure of antibodies. Much of the best work available is in the main an attempt to determine whether the antibodies are proteins, or are substances of unknown constitution which are firmly attached to the proteins. In some respects antibodies have properties similar to the enzymes, and while the structure of enzymes is still unknown, it is noteworthy that two enzymes, urease (19) and pepsin (14), and the enzyme-like substance insulin (6), have been prepared in a crystalline form, and are essentially protein in nature.

The present tendency is to regard antibodies as modified proteins, and the evidence in favor of this protein nature of antibodies has been reviewed by Strumia and coworkers (18), Heidelberger (7) and Wells (21). Locke and Hirsch (10) stated in 1925, "The general belief in the protein containing character of the antibodies is founded on the experimental fact that they may be precipitated with definite protein fractions of the immune serum, and on the theoretical implication that the proteins, alone of the constituents of animal tissue, have the requisite versatility of chemical and spatial configuration to account for the specificity and multiplicity of immunologic reactions". At the present time it is doubtful if either of the two points raised by Locke and Hirsch can be considered valid. If immune-serum proteins are precipitated by different methods, the antibodies do not always follow the same protein fraction. For example, when precipitated by ammonium sulphate, tuberculosis antibodies are found to be practically equally divided between the euglobulin and pseudoglobulin fractions (12, 13). But if euglobulin is precipitated by CO_2 from diluted immune serum, the euglobulin contains little or none of the antibody (8). In fact, there has been so much contradictory evidence as to which protein fractions contain a given antibody, that Mudd (12) refers to it as "the perennial question of the distribution of antibodies amongst serum proteins". Again, recent work on the specific

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polysaccharides of various bacteria by Heidelberger, Avery, Goebel and others (7) indicates that the polysaccharides offer a range of combinations adequate to account for any specific immune properties.

It is possible that many solutions of antibodies have been reported protein-free merely because the chemical tests for proteins are not sufficiently sensitive. On the other hand, antibodies of several types have been purified by Olitzki and Fränkel (15) by means of adsorption on kaolin with subsequent elution, and neither chemical tests nor the exceedingly delicate anaphylactic tests with guinea pigs indicate the presence of protein. The hemolytic antibodies purified by Uchida (20) by specific adsorption on red cells also fail to produce anaphylaxis, although the highly purified hemolytic antibody solutions of Locke and Hirsch (10) produced anaphylaxis when used in sufficiently large quantities. Again, if antibodies are "appropriately modified serum proteins", as Heidelberger (7) suggests, it is strange that they should be unattacked by trysin under conditions which destroy the remainder of serum proteins. This resistance to trypsin was pointed out by Huntoon (9) in the case of pneumococcus antibodies, by Uchida (20) for hemolytic antibodies, and by Pinner (16) for tuberculosis antibodies.

Since the evidence in favor of the protein nature of tuberculosis antibodies is far from conclusive, it appeared desirable to make an examination of immune-serum lipoids, to find if the complement fixing antibodies can under any circumstances be found in this lipoid fraction. Should this be the case, it would make available a simple method of preparing on a large scale antibody solutions which would be almost completely free from protein. This would facilitate the extensive treatment of experimental animals with the antibody preparations, without danger of anaphylactic reactions, and so assist in appraising the clinical value of tuberculosis antibodies.

No adequate data were found in the literature to indicate that the tuberculosis antibodies were of lipoidal nature. Hodge and Maclennan (8) found that when immune human serum was dried on filter paper and extracted with a mixture of alcohol, ether and chloroform, the serum lost its complement fixing power. Their results do not prove whether they had extracted the antibodies into the solvent, or had destroyed them, since the lipoid extracts obtained by this method were so highly anticomplementary that they could not be tested by the complement fixation reaction. It is probable that the method employed had simply destroyed the antibodies, as later work has shown that they can be destroyed by ether (16).

Pinner, in the trypsin digestion experiments to which reference has been made, noted that when toluene was used as an antiseptic the antibodies disappeared from the aqueous solution; he suggested that possibly the antibodies had dissolved into the toluene layer, although his report does not mention any direct examination of the toluene layer for antibodies.

It was obvious from the literature that much of the work concerning the antibodies of tuberculosis had been carried out with serum fractions which, while nominally protein, would also from their method of preparation contain

serum lipoids. For example, Strumia and coworkers (18) have used globulin fractions obtained from immune serum by ammonium sulphate precipitation, although as pointed out by Pinner (16) the lipoids are carried down with the globulin precipitate.

An attempt at the direct extraction of tuberculosis antibodies by means of lipoid solvents is reported by Nishida and Petroff (13). Samples of immune sheep serum were shaken with various solvents, and then held at 37.5° C. for 24 hr. The lipoids so extracted were emulsified in saline, and tested for their complement fixing properties. The authors concluded from their results that the complement fixing antibodies are not lipoids.

Experimental

In order to determine by extraction methods whether the antibodies are of lipoidal nature, three main types of experiment are necessary.

1. *Direct extraction.* This should succeed if the antibodies are in a free state in the serum, and if a suitable solvent and extraction procedure are employed.

2. *Desorption methods.* Should direct extraction fail, it is possible that the antibodies, although normally soluble in the organic solvent employed, are too firmly adsorbed by the serum protein. In this case it should be possible to displace the antibody from the protein by means of some other substance which is still more strongly adsorbed.

3. *Extraction after destruction of the serum protein.* Finally, there is the possibility that the antibodies, although of lipoid nature, are chemically united to the serum protein. In this case, the antibodies would probably be set free after destruction of the serum protein by prolonged trypsin digestion, and should then dissolve in an appropriate lipoid solvent.

The following is an outline of experiments which the writer has carried out by each of these methods.

Direct Extraction

Preliminary experiments were carried out in this laboratory by P. M. Andrus, who duplicated and confirmed the negative findings of Nishida and Petroff to which reference has been made. By quantitative estimation of the lipoids so extracted, Andrus noted that this method was unsatisfactory in that the extraction of lipoids was far from complete; the prolonged contact of the fat solvents with the immune serum—24 hr.—also appeared undesirable. It was obvious that no conclusive results could be obtained without the use of more effective extraction methods. Taking cholesterol and total fatty acids as typical lipoids, various extraction methods were tried, of which the Soxhlet method was found to be the most satisfactory, provided that a suitable inert base was employed. Finely ground sodium sulphate was found to be the most satisfactory inert base, although sodium chloride, powdered

glass, filter paper, and sand can be used. Although plaster is widely used as an inert base, that used by the writer (Baker's c.p. product) gave very poor yields of lipoid during the relatively short extraction periods employed.

Since the thermal death point of the complement fixing antibodies of tuberculosis is about 70° C., only those organic solvents which boil below this temperature could be employed in the ordinary Soxhlet extractor. To increase the range of solvents which could be used, a modified form of the apparatus was constructed which operated under reduced air pressure. This made it possible to adjust the boiling temperatures of a wide variety of solvents to any desired figure by adjusting the degree of vacuum. This vacuum type of extractor is described elsewhere (3).

Table I indicates the efficiency of this Soxhlet apparatus, when operating at reduced temperatures, in extracting fatty acids from sheep serum.

The usual technique for examining serum lipoids was as follows. Immune serum was prepared by intravenous injection of increasing doses of living human-type tubercle bacilli into a sheep. One cubic centimetre of the immune serum, either fresh or inactivated, diluted with 1 cc. of water, was well ground into 30 gm. of anhydrous sodium sulphate (Merck's Blue label). Plaster of Paris was used in place of sodium sulphate in some of the experiments, although as stated above it does not give complete removal of the lipoids. The mixture of serum and inert base was transferred to a large culture tube, covered by a plug of cotton wool, and connected to a high vacuum pump. The lower end of the tube was immersed in a water bath at 50° C. After ½ hr., the contents of the tube was sufficiently dry to be removed and finely ground in a mortar, after which the powder was returned to the tube and dried for an hour longer under high vacuum at 50° C., during which time the tube was well shaken at intervals.

TABLE I

EFFICIENCY OF LOW TEMPERATURE SOXHLET EXTRACTIONS

Inert base	Solvent	Time and temperature of extraction	Fatty acid extracted, mgm. per 100 cc.	Efficiency of the extraction, %
Na_2SO_4	Absolute ethyl alcohol	40 min. at 40° C.	103.4	99.3
Filter paper	Chloroform	40 min. at 40° C.	102.5	98.4
Plaster	Absolute ethyl alcohol	40 min. at 40° C.	73.5	70.5

NOTE.—*The sheep serum used contained 104.2 mgm. of total fatty acid per 100 cc. by Bloor's method (2).*

The dried powder was placed in a paper extraction thimble, and extracted in the Soxhlet extractor to which reference has been made. Ethyl alcohol, both absolute and 95%, methyl alcohol, acetone and chloroform were the

solvents most frequently employed, although methyl acetate, benzol and petroleum ether were also used. Each sample was extracted three times in succession, using fresh solvent each time, with the aim of completely removing the soluble fraction without, however, exposing to prolonged heating the material which was first dissolved. Each of the extraction periods was from 15 to 45 min., while the degree of vacuum was adjusted to cause the solvents to boil at various temperatures from 25° to 50° C.

Each extract was separately placed in a well-cleaned evaporating basin, and placed inside a vacuum desiccator, the latter being inside an incubator at 50° C. When the solvent was completely removed, the evaporating basin was wrapped in paper and stored in the ice box until the tuberculo-complement fixation test was carried out. Immediately prior to the test the sample was emulsified into buffered saline by rubbing with an agate pestle while slowly adding the saline. This gives satisfactory emulsions for extracts obtained by acetone or alcohol. Chloroform extracts usually were redissolved in that solvent, and slowly run into distilled water which was rapidly stirred by a mechanical stirrer. The chloroform was then removed by boiling under high vacuum, and the watery emulsion of lipoids made isotonic with sodium chloride. In the later work, this method of emulsification was used with all extracts, irrespective of the solvent employed for the extraction.

The technique used for the tuberculo-complement fixation test (hereinafter designated as T.C.F. test) was similar to the Petroff technique as detailed by Woolley (22, pp. 160-180) but additional tubes were used containing 2, 2½, 3, 4, 6 and 8 units of complement. The lipoid emulsion which was tested in each tube corresponded to 0.1 cc. of the original immune serum.

Using this technique in the writer's earliest experiments a number of extracts were obtained which gave positive reactions in the T.C.F. test. About 25% of the extracts were too anticomplementary to give useful results. On extending the work by the use of other sheep whose serum had a very much higher titre of antibodies, using immune rabbit and guinea pig serum, and the greatest precautions in technique, it was found impossible to duplicate these early apparently positive reactions. The following are some points of technique which from later experience are believed to have contributed to the apparently positive results obtained at the outset of this work.

1. Where plaster was used as inert base, traces of this carried over into the extract can contribute to non-specific reactions, as shown in recent contributions from these laboratories (4, 5).

2. Emulsifying the lipoid fraction by rubbing up from a porcelain basin is undesirable, as it was observed that the porcelain enamel was easily damaged and that the final emulsion contained fine porcelain particles; this porcelain emulsion alone gives an anticomplementary effect.

3. In the later work the T.C.F. test was modified. Two units of complement were used in each tube, and serial dilutions of the lipoid emulsion were tested. By this dilution method extraneous non-specific factors are minimized.

Extensive work confirmed the conclusion that no true complement fixing antibody was dissolved out by any of the solvents employed. In addition to trying wide ranges of time and temperature for the extraction, the serum was in some experiments adjusted to various pH values from 5 to 9 before drying on the inert base, but in none of these extracts could complement fixing antibodies be detected. Quantitative estimation of the antibody in the extracted protein material remaining in the extraction thimble was attempted in almost all experiments in which sodium sulphate was used as inert base. After drying to remove the organic solvent, sufficient water was added to form at 35° C. a saturated sodium sulphate solution, which was filtered in the incubator. Of the precipitated protein, part was soluble in saline, but most of it was insoluble, due to being denatured, when acetone or alcohol was used as solvent. This insoluble fraction was brought into solution by digestion with a trace of trypsin, and the two protein fractions were separately tested for antibodies. Of 37 of these residual protein samples which were tested, 2 gave positive tests, 3 gave doubtful positive tests, 14 gave negative tests and 18 gave anticomplementary tests. These results give no definite information, as half of the samples are anticomplementary. Quantitative results on the extracted residues were satisfactory only when filter paper or clean sand was used as the inert base, and some solvent such as chloroform was employed, which does not denature the serum protein. Details of this are given below.

Efficiency of Methods Employed

The following trials were carried out to determine whether the methods employed give efficient extraction of lipoids and do not in themselves destroy the antibodies of tuberculosis.

1. *Effect of drying.* (a) Serum dried at 50° C. in vacuum on sodium sulphate is partly denatured, and gave inconsistent results when the recovered serum was tested for antibodies. Serum mixed in the cold with sodium sulphate so as to form a solid mass of $Na_2SO_4 . 10\ H_2O$ crystals, can be recovered with but little loss of the antibodies. Nevertheless, alcohol, acetone and chloroform extracts of serum dried in this manner on sodium sulphate were always negative.

(b) Portions of immune sheep serum were dried on filter paper and on purified sand, while other portions were spread over the bottom of Petri dishes without mixing with any inert base. These samples were dried under various conditions, both exposed to the air and in high vacuum, at various temperatures from 37° to 45° C. In all cases the result was the same, namely, that on redissolving the dried serum, 50% of the original antibody titre remained. Hodge and Maclennan (8) obtained similar results with immune human serum dried on filter paper one hour at 45° C. in air.

2. *Effect of solvent.* Serum dried as above on filter paper or sand was covered with chloroform and allowed to stand one hour at room temperature. The chloroform was then allowed to evaporate, and the serum was recovered

by repeated extraction with saline. Results showed that the treatment with chloroform caused no destruction of antibodies. Similar trials with alcohol or acetone were not carried out, since they denature the serum protein.

3. *Efficiency of extraction methods.* As regards the percentage of total fatty acids extracted, details are given in Table I, and since in examining for antibodies three successive extractions were given, instead of only the one extraction used for the data in this table, it is obvious that the lipoid recovery was very complete.

4. *Recovery of antibodies in protein residue after the extraction.* Immune serum, dried as above on filter paper or sand, was extracted at 40° C. for 30 min. with choroform. The protein residue, after evaporating off the chloroform, was recovered by washing with saline, and showed no loss of antibodies. The chloroform extracts were all negative, as also were extracts in which acetone and alcohol were the solvents. With the last two solvents the antibody titre of the extracted protein could not be determined, as the proteins were denatured. These results are given in Table II, and indicate that all the antibodies, except those lost during the process of drying the serum, remained with the protein fraction.

Other Extraction Methods

Direct extraction methods other than those outlined above were also tried, of which only two examples need be quoted.

TABLE II

EFFECT OF DRYING AND OF ORGANIC SOLVENTS UPON IMMUNE TUBERCULOSIS SERUM

	Titre of antibodies in protein residue, units per cc.	Titre of antibodies in chloroform, acetone or alcohol extract, units per cc.
Serum dried on filter paper, 30 min. at 45° C. in air, then redissolved in saline without extraction by organic solvent	40	—
Serum dried on filter paper as above, then extracted 30 min. at 40° C. with chloroform	40	0
Serum dried on purified sand 1 hr. at 40° C. in air, then redissolved in saline	40	—
Serum dried on purified sand as above, then extracted 30 min. at 40° C. with chloroform	40	0
Serum dried on Na_2SO_4, then extracted with acetone, 30 min. at 40° C.	Protein denatured	0
Serum dried on Na_2SO_4, then extracted with absolute alcohol, 30 min. at 40° C.	Protein denatured	0

NOTE.—*The titre of the fresh serum was 80 units per cc.*

(a) Immune serum was well stirred in a mortar and alcohol or acetone slowly run in, so that the protein was precipitated in a finely divided form. This precipitate was further washed with fresh alcohol or acetone, and allowed to stand in one of these liquids for two hours at various temperatures from 20° to 40° C., the mixture being frequently shaken. In other experiments the precipitated protein was placed in an extraction thimble, and extracted under the reflux condenser of the vacuum extraction apparatus used in the previous experiments. These are not efficient extraction methods, since in all cases only about 80% of the total fatty acids are dissolved out by the solvents. No complement fixing antibodies were found in these acetone and alcohol extracts.

(b) Serum was rapidly stirred by a mechanical stirrer, while chloroform was slowly added, so that a thick white emulsion was formed. After standing for five days at 8° C. the emulsion was cracked by high speed centrifugation. No antibodies were found in the chloroform layer, while the separated serum retained its original titre of antibodies. Only 29% of the total fatty acids had been dissolved out of the serum by the chloroform.

Desorption Experiments

Since direct extraction with lipoid solvents failed to dissolve out the complement fixing antibodies, the following attempts were made to displace antibodies from the serum protein by means of other highly adsorbed substances, benzoic acid and saponin being employed for this purpose. In the recovery of insulin adsorbed upon charcoal, Moloney and Findlay (11) found that benzoic acid in alcoholic solution was the most effective of all the materials they tried for effecting this desorption. Saponin has been also used in experiments of this nature (1, 17).

To reduce the acidity of benzoic acid to that which the antibodies of tuberculosis would safely stand (pH 5.5 to 6.0) aqueous solutions of benzoic acid or mixtures of benzoic acid and sodium benzoate were mixed with immune serum so as to give in several samples a pH range of 5 to 7. Alcohol was then added in excess to completely precipitate the protein. After standing overnight at −10° C. the samples were centrifugated, and the protein residue was stirred for two hours at room temperature with a fresh solution of 50% alcohol containing benzoic acid—sodium benzoate mixture of the same pH as the first supernatant liquid. Both the first and second extracts were neutralized, the alcohol boiled off in a vacuum, and the samples were made isotonic for the T.C.F. test. Control tests showed that the concentration of benzoate employed did not interfere with the serology.

Somewhat similar experiments were made in which saponin was used. To 1 cc. portions of immune serum was added 0.5 cc. of 6% saponin, and then serial amounts of acetic acid were added to the tubes, giving a pH range from 7.6 to 5.2. Alcohol was then added to give a final concentration of 60%, and the samples were kept at −10° C. overnight. The samples were then held at 20° C. for one hour, during which they were frequently shaken, neutralized, concentrated to a small volume and slowly run into a large

volume of acetone at −10° C. to precipitate the saponin. Water was then added to the supernatant liquid, the acetone boiled off in a vacuum, and the samples made isotonic for the T.C.F. test.

Neither of the desorption methods outlined above yielded extracts containing complement fixing antibodies.

Extraction following trypsin digestion

Finally, there remained the possibility that the antibodies were chemically united to the protein, and hence, even if of lipoidal nature, could not dissolve in the organic solvent. To examine this possibility, two experiments were made after trypsin digestion.

(a) A sample of immune-serum globulins, precipitated by ammonium sulphate, was subjected to simultaneous trypsin digestion and dialysis for 48 hr. at 47° C. Most, but not all, of the protein was destroyed, without destruction of the complement fixing power. This material was then dried on purified filter paper, and extracted 30 min. at 40° C. with chloroform in the vacuum extraction apparatus. This extract was completely negative in the T.C.F. test, while the residue on the filter paper, after drying off the chloroform and washing in saline, retained its complement fixing power.

(b) Immune-serum globulins were simultaneously digested with trypsin and dialyzed in flowing water for five days at 37° C.; and the resulting solution retained the antibodies. This solution was practically protein-free since it gave no precipitate on boiling after addition of sodium chloride and acetic acid; sulphosalicylic acid gave no immediate precipitate, although a slight sediment settled out after standing overnight. The digested sample was dried on purified plaster of Paris, and extracted in the vacuum type of Soxhlet apparatus with 95% alcohol for 30 min. at 45° C. The extract contained no complement fixing antibodies. Pinner (16) had noticed that if immune serum is covered with toluol while undergoing trypsin digestion, the antibodies disappear from the water phase. He tentatively suggested that the antibodies might have dissolved into the toluol layer. However, in attempting to use a wide variety of antiseptics (borate, salicylate, benzoate, chloroform, toluol, thymol, camphor, phenol) to prevent contamination of a trypsin digest of immune tuberculosis serum, the writer has always found that the antibody was destroyed by the joint action of trypsin and antiseptic. Pinner's result is apparently due to destruction of antibody by toluol plus trypsin, and not an indication that the antibodies are soluble in the toluol.

Discussion

The results of this work confirm the viewpoint that the antibodies of tuberculosis are not of lipoidal nature, since all the solvents and extraction methods tried, even after trypsin digestion of the serum protein, gave negative results. Further study of the chemical nature of these antibodies should apparently be directed either to those proteins which are resistant to trypsin, or possibly to the polysaccharides.

It is probable that the resistance of antibodies in general to trypsin digestion is related to the fact that many bacteria secrete proteoclastic enzymes. The function of an antibody apparently is to unite with its homologous organism, and in so doing modify its surface properties so as to facilitate humoral or cellular bacteriolysis. Obviously, any antibody which could be destroyed by its homologous micro-organism would be very ineffective.

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VIBRATIONS IN SOLID RODS AND DISKS[1]

By Geo. S. Field[2]

Abstract

I. A method is described for producing on the screen of a cathode ray oscillograph a curve showing the oscillations occurring in a solid rod or disk as the result of impact. These curves are usually quite complex, as they represent combinations of several different modes of vibration. They may be analyzed, however, so that for any specimen the various component frequencies may be determined. This has been done for a great number of rods and disks, and the experimental frequencies so obtained have been compared with those calculated from theory. A discussion of the results is given.

II. The solutions given by Love (5, p. 291) for the general equations of vibration applicable to transverse waves in cylindrical rods are examined, and it is shown that they do not apply to comparatively short rods. Other solutions of the same simple form are considered, and the conclusion is finally reached that a much more complex solution will be required to satisfy all the boundary conditions.

PART I

Introduction

The propagation of ultrasonic vibrations in solid rods has recently attracted considerable attention, and both theoretical and experimental work have been done to show the influence of frequency on the phase velocity of the longitudinal and flexural vibrations. The experimental method of analysis usually employed involves setting the rod into mechanical vibration by means of magnetostrictive or piezo-electric coupling with an electric oscillator. The resonant frequencies of the rod are found, the wave-length determined and a calculation then made of the wave velocity (1, 2, 6, 7, 8).

Recently a somewhat different method of studying vibrations in rods was devised, which shows in a quantitative way the numerous vibrations which may occur at the same time in a solid rod, and a short account of the technique was published (3). In this paper the apparatus is described more fully, and the results obtained so far are given and discussed.

Experimental

Utilizing the apparatus shown schematically in Fig. 1, the rod being studied is tapped at one end with a small hammer ten times a second. The resulting damped wave-trains in the solid are picked up by a small piece of piezo-electric quartz, cemented to one end. The slight e.m.f. appearing on the crystal is amplified by a six-stage, resistance-capacity-coupled amplifier and eventually appears across the plates of a cathode ray oscillograph, which has in connection with it a properly synchronized time-axis device. Synchronization is effected by having the hammer close an electrical circuit, which makes the grid of the thyratron go positive, each time the hammer hits the rod,

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the result being that the condenser in parallel with the discharge tube discharges and immediately begins to charge again through the diode in series with it. The potential across the condenser steadily rises, and being impressed on the horizontal deflection plates of the oscillograph, causes the wave-train under examination to be drawn out as a curve with a time base on the oscillo-

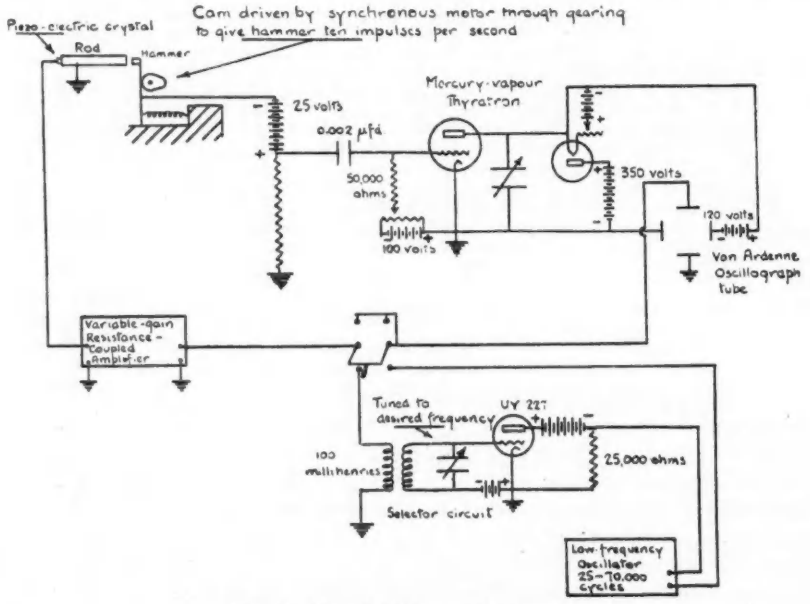

FIG. 1. *Schematic diagram of apparatus.*

graph screen. Each wave-train is exactly superposed on the one preceding, so that a steady picture is obtained, representative of the periodic displacements of the end of the rod with time.

In general the waves are very complex, being composed of frequencies from several modes of vibration. This complexity has previously been qualitatively observed by other workers (2) at high frequencies. To separate the various components, the voltage from the amplifier is passed through a tuned circuit, and the selected frequency then impressed on the oscillograph. To measure the frequencies thus separated, a heterodyne method is used. The selected frequency is combined with the output from a continuous-wave oscillator, and beats obtained on the oscillograph screen. Originally an aural method of detecting the beats was tried, but the wave-trains are of such short duration that the beat note was obscured by the clicks of the ten wave-trains per second. In the procedure employed, the frequency of the oscillator is varied until zero beat is observed on the screen; this frequency is measured with a wave-meter, and the frequency of the selected component from the complex wave-train is thus also known.

For each wave-train examined, *i.e.*, for every rod, the selector circuit was tuned over the whole band of frequencies from about the lowest fundamental of the rod to a frequency above which the overtones were too weak to be noticed. In this way the fundamentals and overtones of the different modes of vibration for each rod or disk were sorted out and their frequencies measured.

Results

General

In Fig. 2 are shown the various frequencies occurring in rods of duralumin, 6.50 cm. diameter, for lengths from 0.5 to over 40 cm. Curves have been drawn through the plotted points and these curves have been lettered to indicate the mode of vibration which they apparently represent. *F* signifies flexural, and *L*, longitudinal vibrations. The subscript *f* indicates the fundamental mode and the subscripts *1*, *2*, *3*, etc., the first, second, third and higher overtones. P_1 and P_2 are what have been called in this paper the "plate" frequencies, and C_1 is the "constant" frequency. As far as is known this is the first time these last three types of vibration have been observed in rods. These various modes will be discussed in detail later.

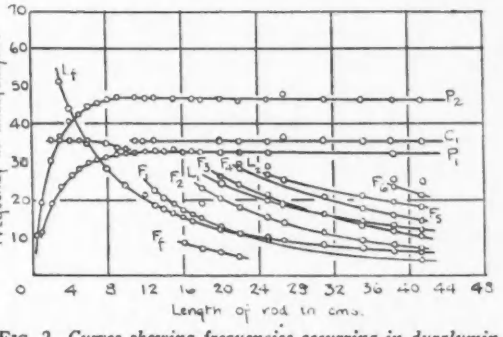

FIG. 2. *Curves showing frequencies occurring in duralumin rods, 6.50 cm. in diameter.*

By referring to the curves, it will be observed that the flexural and longitudinal frequencies did not normally appear at frequencies greater than about 30 kilocycles. For very short rods (approaching disk characteristics), the fundamental longitudinal vibration was observed up to just over 50 K.C., but for what might really be called "disks" or "plates" only the plate frequencies appeared.

Importance of Point of Impact

Contrary to expectations, within limits, the point where the rod was hit did not appear to make a great deal of difference. It was found that if the rod were struck perpendicularly to the long axis, on the side near one end, the flexural vibrations were very prominent, and the longitudinal ones were weak or absent; but if the impact were anywhere on the end face, the longitudinal and flexural modes appeared with amplitudes nearly independent of the angle at which the hammer struck or the actual point of impact.

Working with disks of large diameter, *i.e.*, 10 cm., it was found that more frequencies appeared if the disk were hit slightly off centre than if the impact occurred exactly at the centre.

With these slight exceptions, the point of impact was not very important in determining whether certain frequencies would or would not appear.

Longitudinal Vibrations

It was hoped originally that the fundamental longitudinal mode would appear for the very short rods, so that wave velocities could be calculated for fairly high frequencies, but as the rods were shortened, the longitudinal vibration disappeared, and hence these calculations could not be made. It has therefore, by this method, not been possible so far to obtain wave velocities for very large values of the ratio, $\frac{\text{radius of rod}}{\text{length of rod}}$ (2), as it had been hoped to do at the beginning of this work.

Flexural Vibrations

The frequencies of the flexural vibrations corresponding to different lengths of rod have been re-plotted in Fig. 3. In the same figure have been drawn lines representing the frequencies of the different flexural modes of a free-free bar, using the theoretical relation between frequency and length of bar as given by Lamb (4, p. 126), *i.e.*, $f = \frac{K\pi}{2} \cdot \frac{k^2}{l^2} \cdot \sqrt{\frac{E}{\rho}}$, where f = frequency, K = radius of gyration of cross-sectional area, $k = s + \frac{1}{2}$, approximately, where s = an integer, l = length of rod, E = Young's modulus and ρ = density. It will be seen that the theoretical and experimental curves agree for the graver modes for long rods, but as the overtones become higher or the length of rod decreases, the two sets of curves separate widely.

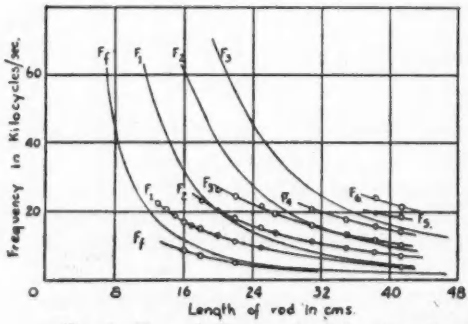

FIG. 3. *Flexural vibrations for different lengths of duralumin rods, each 6.50 cm. in diameter.*

In the derivation of the theoretical frequency equation, certain simplifications were introduced which make the equation applicable only to rods where the wave-length is large compared with the radius. This explains the discrepancy between the theory and experiment.

The equations given by Love (5, p. 288), however, should apply to rods of any radius, and recent experimental work* by Röhrich (10) seems to confirm this for rods when the wave-length of the vibration is small compared with the length. When this last restriction is removed, however, the solutions given by Love for the general equations do not seem adequate, apparently because such solutions are not sufficiently complete. In Part II it will be shown that no solution of the form suggested will satisfy the boundary conditions, one much more complicated apparently being required.

**Although Röhrich did not compare his experimental work with the theory given by Love and amplified by Ruedy (12), if such be done it will be found that the agreement is as good as can be expected.*

Plate Vibrations

In Figs. 4, 5, and 6 are shown the plate frequencies plotted for short rods of duralumin of diameters 5, 6.5 and 10 cm. They have been referred to as "plate" vibrations because it is believed that they represent the two normal modes which are usually considered in the theory of the vibrations of a free circular disk. This seems likely because they were the only modes appearing for very thin disks, and the variation of frequency with length for thin disks was linear as predicted by theory. It is suggested that P_1 is the gravest of the normal modes, having two nodal diameters and no nodal circle. P_2 would then be the mode having no nodal diameter and only one nodal circle.

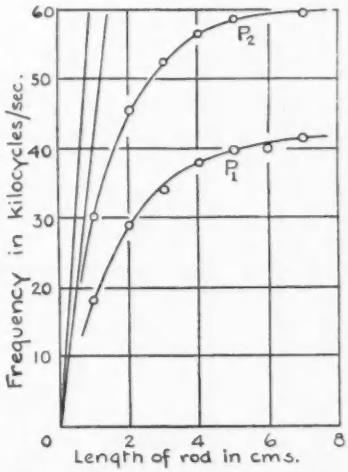

FIG. 4. *Plate frequencies for duralumin rods, 5 cm. in diameter.*

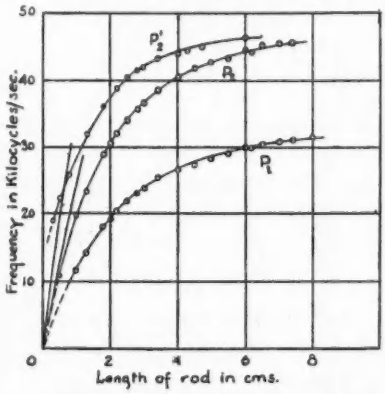

FIG. 5. *Plate frequencies for duralumin rods, 6.50 cm. in diameter.*

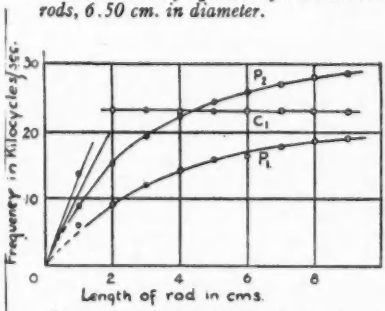

FIG. 6. *Plate frequencies for duralumin rods, 10.0 cm. in diameter.*

For the disks of duralumin these frequencies were very strong, becoming weaker as the thickness of disk increased. It is, however, remarkable that such vibrations could be detected for rods over 40 cm. long. It is also worth noting that these frequencies are unchanged for different lengths of rod after the "very short rod" stage has been passed.

In Fig. 7 it is shown that by plotting the product of length of rod (l) and frequency (n) against l, a straight line is obtained, except for a slight deviation near the origin.

By means of the theoretical formulas due to Poisson, Kirchoff, etc., and summarized by Lamb (4, pp. 155–156), the frequencies of the two gravest modes of free vibration in a circular plate have been calculated for various thicknesses. They are represented in Figs. 4, 5 and 6 by the straight lines going through the origin. In deriving these formulas, the assumption is always made that the plates are very thin; hence the results can be used only when this is true. For this reason, the

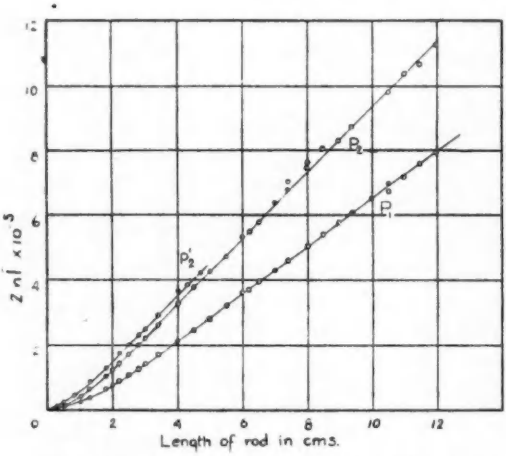

FIG. 7. *Showing straight lines obtained by plotting 2nl against l.*

experimental curves cannot be expected to agree with the theoretical ones over very much of their length. They should, however, become tangent to them for lengths of rods approaching zero. From the graphs, it appears that they do not do so, and the following analysis shows this to be true.

It has been found that the experimental plate frequencies are given by the empirical expressions,

$$f_1 = A_1/a\left(1 - e^{-\frac{k_1 l}{a}}\right),$$

$$f_2 = A_2/a\left(1 - e^{-\frac{k_2 l}{a}}\right),$$

where f_1 and f_2 are the observed plate frequencies; A_1, A_2, k_1, k_2 are constants; l is the length of the rod and a the radius.

When l is small, these equations reduce to,

$$f_1 = A_1 k_1 l/a^2,$$
$$f_2 = A_2 k_2 l/a^2.$$

If the values for the A's and k's, as determined for duralumin, be filled in, we obtain,

$$f_1 = 1.50 \times 10^5 \cdot l/a^2 = 0.288\, l/a^2 \sqrt{\frac{E}{\rho}}$$

$$f_2 = 2.66 \times 10^5 \cdot l/a^2 = 0.512\, l/a^2 \sqrt{\frac{E}{\rho}}\,.$$

The values for f_1 and f_2, according to Kirchoff and Poisson, as given by Lamb (4, p. 155-156), are,

$$f_1 = 0.517\ l/a^2 \cdot \sqrt{\frac{E}{\rho}}$$

$$f_2 = 0.88\ \ l/a^2 \cdot \sqrt{\frac{E}{\rho}}\,.$$

It will be seen that the calculated values for f_1 and f_2 are very different from those which have been found experimentally. It may be that the observed frequency, f_2, corresponds to the theoretical one, f_1, but the difficulty in this assumption is that the observed frequency, f_1, is not then accounted for at all by the theory, which indicates that no mode graver than the theoretical f_1 is to be expected.

Underlying the above argument there was the assumption that the equations, $f = A/a\left(1 - e^{-\frac{kl}{a}}\right)$, would apply for plates thinner than those on which

observations were made. It might be argued that the theoretical relations are valid only for very thin plates (thinner than those examined experimentally), and that if observations had been made on such very thin disks, better agreement would have resulted. Upon examining the graphs, however, it will be seen that for the experimental curves ever to become tangent to the theoretical ones a most improbable lateral shift of such curves would be required.

Effect of the Crystal Detector on the Plate Frequencies

Originally a slab of tourmaline, 0.5 cm. thick, covering most of the end of the rod, was employed as a detector, but it was felt that probably the frequencies of the normal modes were being altered considerably by having such a heavy mass cemented to the rod. Accordingly, smaller and smaller pieces of crystal were successively tried, until no change in the frequency of the vibration resulted from further decreasing the size of the detector. The crystal finally used was quartz, 0.257 cm. thick, having an area of about 2.6 cm.^{2}, *i.e.*, covering about 8% of the end area of the rods that were 6.5 cm. in diameter. It was found that the frequencies were five to ten kilocycles higher for the tourmaline on the end of the rods than for the thin quartz.

The effect of the detector on frequency is shown in Fig. 5, where the curve P_2 is for the small piece of quartz and the curve P'_2 for the comparatively heavy detector of tourmaline. It will be noticed that the curve P'_2 approaches the curve P_2 for long lengths of rod, and that the straight line obtained by plotting $2nl$ against l for P'_2 in Fig. 7 is parallel to the straight line obtained in a similar way for P_2. These two facts simply imply that the tourmaline increases the effective length of the rod, which is of course the result one would expect.

Constant Frequency Vibrations

These vibrations, having frequencies independent of length of rod, were observed for duralumin rods and disks of diameters 10.0 and 6.5 cm., but not for the 5.0-cm. rod. In the latter case, the "constant frequency" vibrations were probably at a fairly high frequency, and it was found that in general vibrations did not appear if they were to be expected at frequencies high in comparison with those of the lower modes.

For 10-cm. rods the frequency C_1 had a value of 23.2 K.C., and for the 6.5-cm. rods the frequency was about 35.5 K.C. These frequencies are inversely proportional to the diameter of the rods, so that we can write for them, $f_{c_1} = K/d$, where f_{c_1} is the frequency, d the diameter of the rod and K a constant, presumably depending on the material of which the rod is composed.

Just where these modes of vibration have their origin is not definitely known. It is possible that they are radial vibrations, which affect the crystal at the end of the rod by means of the coupling which exists between the various degrees of freedom. The theoretically calculated frequencies (11) of the fundamental modes of radial vibration for the two cases (10.0 and 6.5 cm.

diameter) are, however, 44.6 and 70.2 K.C., which are almost exactly double the frequencies C_1. It may be that the theory is in error, and that these frequencies really do arise in a radial vibration, for it is significant that the C_1 vibrations are dependent on the radius and independent of the length. Since the theoretical frequencies bear the 2 : 1 ratio to the experimental ones, it was at first thought that a factor of 2 might have been dropped somewhere in the theory, but examination has failed to reveal any mistakes of this nature.

Other Metals Tried

A few rods of copper and lead were examined, and the observed frequencies compared with those calculated from theory.

With the lead rods so many frequencies appeared that it was not found possible to sort them out and ascribe them to the correct modes of vibration. It was difficult to understand how so many could arise in the known degrees of freedom, unless the velocity of sound in the material were much lower than that usually quoted and the frequencies observed represented a great many of the higher overtones. No satisfactory explanation for this difficulty with lead rods has been found.

PART II

Introduction

Since the simple equation for transverse vibrations in rods given by Lamb (4, p. 126) was found not to agree with the experimental results, an examination was made of the more complete theory given by Love (5, p. 291) to see if it would explain the results obtained in this investigation for comparatively short rods.

General Equations of Vibration

The equations of vibration (5, p. 288) referred to cylindrical co-ordinates are,

$$\alpha^2\left[\frac{\partial^2 u_r}{\partial r^2}+\frac{1}{r}\frac{\partial u_r}{\partial r}-\frac{1}{r^2}\frac{\partial u_\theta}{\partial \theta}-\frac{u_r}{r^2}\right]+\beta^2\left[\frac{\partial^2 u_z}{\partial r\,.\,\partial z}+\frac{1}{r}\frac{\partial^2 u_\theta}{\partial r\,.\,\partial \theta}\right]$$
$$+\gamma^2\left[\frac{\partial^2 u_r}{\partial z^2}+\frac{\partial^2 u_z}{\partial r\,.\,\partial z}+\frac{1}{r}\frac{\partial^2 u_\theta}{\partial r\,.\,\partial \theta}-\frac{1}{r^2}\frac{\partial u_\theta}{\partial \theta}+\frac{1}{r^2}\frac{\partial^2 u_r}{\partial \theta^2}\right]=\frac{\partial^2 u_r}{\partial t^2}$$

$$\alpha^2\left[\frac{1}{r^2}\frac{\partial^2 u_\theta}{\partial \theta^2}+\frac{1}{r^2}\frac{\partial u_r}{\partial \theta}\right]+\beta^2\left[\frac{1}{r}\frac{\partial^2 u_z}{\partial \theta\,.\,\partial z}+\frac{1}{r}\frac{\partial^2 u_r}{\partial \theta\,.\,\partial r}\right]$$
$$+\gamma^2\left[\frac{\partial^2 u_\theta}{\partial z^2}+\frac{\partial^2 u_\theta}{\partial r^2}+\frac{1}{r}\frac{\partial^2 u_z}{\partial \theta\,.\,\partial z}+\frac{1}{r}\frac{\partial u_\theta}{\partial r}-\frac{u_\theta}{r^2}+\frac{1}{r^2}\frac{\partial u_r}{\partial \theta}+\frac{1}{r}\frac{\partial^2 u_r}{\partial \theta\,.\,\partial r}\right]=\frac{\partial^2 u_\theta}{\partial t^2}$$

$$\alpha^2\frac{\partial^2 u_z}{\partial z^2}+\beta^2\left[\frac{\partial^2 u_r}{\partial r\,.\,\partial z}+\frac{1}{r}\frac{\partial^2 u_\theta}{\partial \theta\,.\,\partial z}+\frac{1}{r}\frac{\partial u_r}{\partial z}\right]$$
$$+\gamma^2\left[\frac{1}{r}\frac{\partial u_r}{\partial z}+\frac{\partial^2 u_r}{\partial r\,.\,\partial z}+\frac{\partial^2 u_z}{\partial r^2}+\frac{1}{r}\frac{\partial u_z}{\partial r}+\frac{1}{r}\frac{\partial^2 u_\theta}{\partial \theta\,.\,\partial z}+\frac{1}{r^2}\frac{\partial^2 u_z}{\partial \theta^2}\right]=\frac{\partial^2 u_z}{\partial t^2}$$

where $\alpha^2=\dfrac{\lambda+2\mu}{\rho}$, $\beta^2=\dfrac{\lambda}{\rho}$ and $\gamma^2=\dfrac{\mu}{\rho}$

The stress components are,

$$\widehat{r\theta} = \gamma^2\rho\left[\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} + \frac{1}{r}\frac{\partial u_r}{\partial \theta}\right] \qquad \widehat{zr} = \gamma^2\rho\left[\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right]$$

$$\widehat{z\theta} = \gamma^2\rho\left[\frac{\partial u_\theta}{\partial z} + \frac{1}{r}\frac{\partial u_z}{\partial \theta}\right] \qquad \widehat{zz} = \alpha^2\rho\frac{\partial u_z}{\partial z} + \beta^2\rho\left[\frac{\partial u_r}{\partial r} + \frac{1}{r}\frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r}\right]$$

$$\widehat{rr} = \alpha^2\rho\frac{\partial u_r}{\partial r} + \beta^2\rho\left[\frac{\partial u_z}{\partial z} + \frac{1}{r}\frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r}\right].$$

As a solution of the general equations, applicable to the case of transverse vibrations, the following is suggested by Love (5, p. 291) for the particle displacements,

$$(u_r, u_\theta, u_z) = (U\cos\theta, V\sin\theta, W\cos\theta)\, e^{i(\delta z + pt)}$$

where U, V and W are functions only of r.

Now δ may be real or imaginary, so that (u_r, u_θ, u_z) may be either circular or real exponential (which includes hyperbolic) functions of z. It will be shown later that by virtue of the boundary conditions they must be either one type of function or the other; they cannot be combinations of real exponential and circular functions.

Let us consider these two cases, to determine which, if either, is applicable to the present problem.

1. Real Exponential or Hyperbolic Function of z

For this solution the vibrating rod may take up the forms given by the curves e^{-kz}, e^{+kz}, sinh kz or cosh kz. For a wave travelling down a long rod, nodes are experimentally observable at distances one-half wave-length apart. Obviously the forms for the curve taken up by the rod as given by the above suggested functions could not give such a series of nodes. While such curves for a finite rod are conceivable for the gravest mode of free vibration, no overtones are then theoretically possible.

It may also be shown that such solutions do not satisfy the boundary conditions at $z=0$ and $z=l$. For such values of z we must have $\widehat{zz} = \widehat{z\theta} = \widehat{zr} = 0$.

$$\widehat{zz} = \left[\alpha^2\rho W\frac{\partial f_1(z)}{\partial z} + \beta^2\rho\left(\frac{\partial U}{\partial r}\cdot f_2(z) + \frac{V}{r}\cdot f_2(z) + \frac{U}{r}\cdot f_2(z)\right)\right]\cos\theta$$

where $f_1(z), f_2(z), f_3(z) = e^{\pm kz}$, cosh kz or sinh kz.

Try $f_1 = \cosh kz, f_3 = f_2 = \sinh kz$.

Then, $\widehat{zz} = \rho\left[\alpha^2 kW + \beta^2\left(\frac{\partial U}{\partial r} + \frac{U+V}{r}\right)\right]\cos\theta\sinh kz \begin{cases} = 0, \text{ for } z = 0 \\ \neq 0, \text{ for } z = l. \end{cases}$

$$\widehat{z\theta} = \gamma^2\rho\left(kV - \frac{W}{r}\right)\sin\theta\cosh kz \neq 0, \text{ for } z = 0 \text{ or } l.$$

Also, $\widehat{zr} \neq 0$, for $z = 0$ or l.

It may be shown that none of the suggested forms for $f_1(z)$ and $f_2(z)$ can make the stress components vanish at the boundary.

2. Circular Functions of z

The rod may take up the forms given by the curves cos kz or sin kz. This solution will account for overtones and indicates a series of nodes for a wave travelling down a rod.

Consider the boundary conditions, assuming that $f_1(z) = \cos kz$ and $f_2(z) = \sin kz$.

$$\widehat{zz} = \rho \cos\theta\left[-\alpha^2 kW + \beta^2\left(\frac{\partial U}{\partial r} + \frac{U+V}{r}\right)\right] \sin kz = 0, \text{ for } z = 0 \text{ and } l, \text{ if } k = \frac{n\pi}{l}.$$

$$\widehat{z\theta} = \gamma^2\rho\left(kV - \frac{W}{r}\right) \cos kz \sin\theta \neq 0 \text{ for } z = 0 \text{ and } l, \text{ with } k = \frac{n\pi}{l}$$

It may also be shown that $\widehat{zr}$ will not vanish at the ends of the rod.

For a very long cylinder, *i.e.*, long in comparison with the distance between nodes, the fact that all the stress components do not vanish at the ends may probably be neglected, since it is likely that only a small portion of the rod near each end will be affected. This conclusion has been born out by experiment (10). When this is true, the phase velocity of the wave in the rod is given by the relation, $c = f\lambda = \frac{2lf}{n}$, where f is the frequency of the nth mode.

If this relation be used to calculate velocities from the data obtained for short and medium rods in this research, Fig. 8 is obtained. The theoretical curve based on the above has been drawn in, and the experimental values obtained have been plotted. Each series of points connected by the curves is for a certain mode of vibration, the first, second, third, etc. It will be seen that as the overtones get higher the theoretical velocity curve is more and more closely approached, but for the first few modes the agreement is very poor.

From these results it is clear that solution No. 2 is not applicable to short or medium rods, that is, rods whose lengths are comparable with the distance between successive nodes, though it is sufficiently accurate for long ones. In the theory given by Rayleigh (9) and Lamb (4, p. 126), the particle displacements are found to be combinations of hyperbolic and circular functions of z, *i.e.*, $u_z = A(\cos mz + \cosh mz) + B(\sin mz + \sinh mz)$. The nodes near the ends are then not an equal distance apart, but near the middle of the bar the spacing is uniform. This explains the experimental result depicted in Fig. 8, that when the rod is long and the overtones are high (so that most of the nodes may be considered remote from the

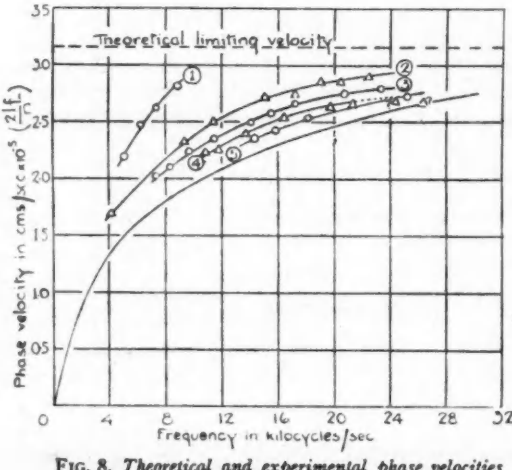

FIG. 8. *Theoretical and experimental phase velocities of flexural vibrations in 6.50 cm. diameter duralumin rods.*

ends), very little error is introduced by considering all the nodes equally spaced, that is, assuming that the displacement of the particles in the rod is given by a sine function. When the number of nodes is small, however, most of the nodes are not equally spaced, the displacement of points on the rod cannot be represented by a sine function, and hence the calculations of phase velocity depending on this hypothesis are not valid.

It will now be shown that the general equations of vibration cannot have a solution applicable to a cylindrical rod of the form,

$$(u_r, u_\theta, u_z) = (U\cos\theta, V\sin\theta, W\cos\theta)\, f(z)\, e^{ipt},$$

where $f(z)$ is a combination of both hyperbolic and circular functions. It will also be shown that if each of (u_r, u_θ, u_z) can be expressed as $F_1(\theta) \cdot F_2(r) \cdot F_3(z) \cdot e^{ipt}$, that is, products of functions, each of which is a function only of r, θ or z, then $F_3(z)$ must be a real or imaginary exponential function.

Let us take,

$$(u_r, u_\theta, u_z) = U\cos\theta . F_1(z),\ V\sin\theta . F_2(z),\ W\cos\theta . F_3(z) . e^{ipt}.$$

Only one of the general equations need be considered, *i.e.*,

$$\alpha^2\left[\frac{\partial^2 U}{\partial r^2} + \frac{1}{r}\frac{\partial U}{\partial r} - \frac{U}{r^2}\right] F_1 - \alpha^2 \cdot \frac{V}{r^2} \cdot F_2 + \beta^2\left[\frac{\partial W}{\partial r} \cdot \frac{\partial F_3}{\partial z} + \frac{1}{r}\frac{\partial V}{\partial r} \cdot F_3\right]$$
$$+ \gamma^2\left[U\frac{\partial^2 F_1}{\partial z^2} + \frac{\partial W}{\partial r} \cdot \frac{\partial F_3}{\partial z} + \left(\frac{1}{r} \cdot \frac{\partial V}{\partial r} - \frac{V}{r^2}\right) F_2 - \frac{1}{r^2} \cdot UF_1\right] = -p^2 UF_1 \qquad (1)$$

At $r=a$, the conditions $\widehat{zr}=0$, and $\widehat{rr}=0$ must be satisfied;

that is, $$\left(U(a) \cdot \frac{\partial F_1}{\partial z} + \frac{\partial W}{\partial a} \cdot F_3\right)\cos\theta = 0 \qquad (2)$$

and $$\left[\alpha^2 \frac{\partial U}{\partial a} \cdot F_1 + \beta^2\left(W(a)\frac{\partial F_3}{\partial z} + \frac{F_1}{a}\right)\right]\cos\theta = 0 \qquad (3)$$

Of course, the general equation (1) must hold also for $r=a$.

From (2), since $U(a)$ and $\dfrac{\partial W}{\partial a}$ are not in general each zero, we must have

$$\frac{\partial F_1}{\partial z} = k_1 F_3, \text{ so that then } \left(k_1 U(a) + \frac{\partial W}{\partial a}\right) = 0.$$

From Equation (3), likewise,

$$\frac{\partial F_3}{\partial z} = k_2 F_1.$$

Substituting for $\dfrac{\partial F_3}{\partial z}$ in (1), we get,

$$\alpha^2\left[\frac{\partial^2 U}{\partial r^2} + \frac{1}{r}\frac{\partial U}{\partial r} + \left(\frac{p^2}{\alpha^2} - \frac{\alpha^2+\gamma^2}{\alpha^2} \cdot \frac{1}{r^2}\right) U + (\beta^2+\gamma^2) k_2 \frac{\partial W}{\partial r}\right] F_1$$
$$+ \left[(\beta^2+\gamma^2)\frac{1}{r}\frac{\partial V}{\partial r} - (\alpha^2+\gamma^2)\frac{V}{r^2}\right] F_2 + \gamma^2 U \frac{\partial^2 F_1}{\partial z^2} = 0 \qquad (5)$$

The coefficient of $\frac{\partial^2 F_1}{\partial z^2}$ cannot be zero, since for $U=0$, there would be no movement radially of the particles in the rod, and for a transverse vibration such must occur.

The coefficient of F_2 might be zero, in which case we should have $V=Cr^n$, where C is a constant of integration and $n=\frac{\alpha^2+\gamma^2}{\beta^2+\gamma^2}$. If, however, one of the other equations, *e.g.*, Equation 3, be considered, it will be found that some other function of V would be required to make the coefficient of F_2 vanish. Hence, in Equation 5, the coefficients of neither F_2 nor $\frac{\partial^2 F_1}{\partial z^2}$ can be made to vanish individually, so that we must have,

$$F_2 = k_3 F_1 \quad \text{and,} \quad \frac{\partial^2 F_1}{\partial z^2} = k^2_4 F_1.$$

The solution of this last equation is $F_1=Ae^{k_4 z}+Be^{-k_4 z}$, where k_4 may be either real or imaginary, since k_4 is an undetermined constant. It will be seen that a solution cannot exist of the form $Ae^{\pm k_4 z}+Be^{\pm i k_4 z}$, which means that F_1 cannot be a combination of both circular and hyperbolic functions.

The above results show that if (u_r, u_θ, u_z) can be expressed as products of functions, each of which is a function only of r, θ or z, then $F_1(z)$ must be an exponential function with either real or imaginary argument. It has previously been shown that neither of these two cases leads to a solution of the general equations which is applicable to the case of transverse vibrations in short rods, and therefore it has been proved that (u_r, u_θ, u_z) cannot be expressed as products of separable functions of the three variables. It appears, therefore, that a more complex solution is required.

It is possible that functions of the form, $r^q(r-a)^m z^s(z-l)^n F_1(r,z)\, F_2(\theta)$ might be determined which would fit the various equations, but it appears that to find suitable solutions would be very difficult. If general solutions could be determined, it is probable that all the modes of vibration determined experimentally in this investigation, for some of which it has been difficult to account theoretically, might be explained.

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AN ELECTROSTATIC VOLTMETER FOR HIGH VOLTAGES[1]

By Geo. S. Field[2]

Abstract

An electrostatic voltmeter which is of fairly simple construction is described. It has a scale which is more nearly linear than is usually found with such instruments, and which can be applied to several different voltage ranges.

The essential parts of the instrument are shown schematically in Fig. 1. S_1 is a fixed duralumin ball, 15.2 cm. in diameter; S_2 is a light celluloid ball, 3.8 cm. in diameter, covered with aluminium paint. To S_2 is attached a small shaft (shown at a), which is pivoted in jewel bearings. W_1 and W_2 are weights, the first being used to adjust the sensitivity of the moving element, and the second to correct the zero position of the pointer, P, which is of thin glass and is easily removable.

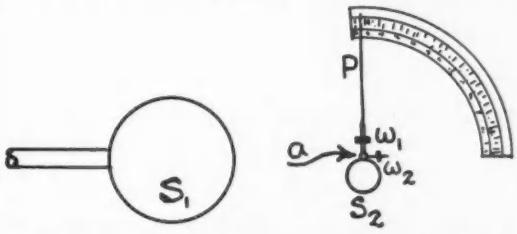

Fig. 1. *Diagram showing arrangement of instrument parts.*

The ball S_1 is attached to a duralumin rod, fitted into a sleeve, so that it may be moved towards and away from S_2. S_1 is connected to the high potential. The support which holds the jewel bearings, and hence the moving element, is connected to ground. In order that S_2 may also be grounded, a very fine, loosely coiled piece of gold wire connects it to the support. The housing consists of a mahogany box, fitted with a window through which the moving element may be watched. A photograph of the complete instrument is shown in Fig. 2.

If E be the potential difference between the two balls, the force tending to draw them together is kE^2/d, where k is a constant and d is the distance between their centres. In this expression the distortion of the electric field as the result of other material, *e.g.*, the metal frame holding up the moving element, being in the neighborhood of S_1 and S_2 is neglected. If l be the distance from the centre of S_2 to the axis of the moving element, and if θ be the angle through which S_2 has turned about this axis, the torque tending to rotate S_2 is $(kE^2/d^2)\ l \cos\theta$.

Fig. 2. *Photograph of completed instrument.*

If m be the mass of the moving element, and t the distance of the

[1] *Manuscript received April 12, 1933.*
Contribution from the National Research Laboratories, Ottawa, Canada.

[2] *Junior Research Physicist, National Research Laboratories, Ottawa.*

centre of gravity from the axis, the balancing torque due to the weight of the element is $mgl \sin\theta$, where g is the acceleration due to gravity.

When the element comes to rest, therefore,

$$(kE^2/d^2)\, l \cos\theta = mgl \sin\theta,$$

or,

$$E^2 = K d^2 \tan\theta, \qquad (1)$$

which is the equation of the meter.

In Fig. 3 curves have been drawn through points plotted from experimental results. Curve 1 is for the two balls, 23·5 cm. apart, and Curve 2 is for the balls 49·5 cm. apart. From one point on Curve 1, the corresponding relation between E and θ was used to determine K in Equation (1). The broken curve was then drawn by using the theoretical relation. Using the same equation, with the appropriate d supplied, the second broken curve was drawn. That the electric field is considerably distorted is shown by the discrepancy between the theoretical and experimental curves. In the second case the agreement is better, which suggests that the field becomes more regular as the spheres are separated.

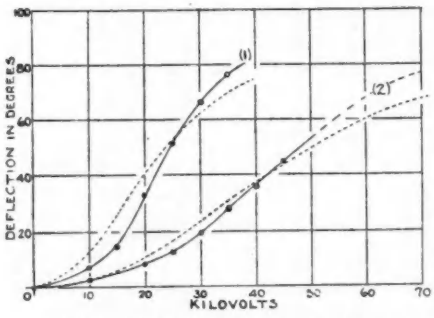

FIG. 3. *Theoretical and experimental curves.*

In Fig. 4 is shown a facsimile of the scale of the meter for the two calibration curves mentioned above. As voltages above 45,000 were not available, it was not possible actually to calibrate above that voltage. However, probable scale divisions have been drawn in, based on an extrapolation of Curve 2. It will be seen that the scale is much more linear than is usually obtained with electrostatic voltmeters, and that if the theoretical curves could be more closely approached, even greater linearity would be obtained.

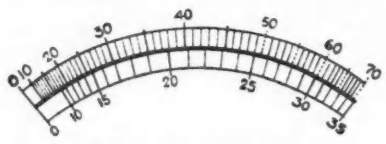

FIG. 4. *Instrument scales.*

THE SOLUBILITY OF LIME IN WATER AND THE SPECIFIC CONDUCTIVITIES OF ITS SATURATED SOLUTIONS[1]

By A. D. Grieve,[2] G. W. Gurd,[3] and O. Maass[4]

Abstract

The specific conductivities of saturated solutions of calcium hydroxide have been measured from 0° to 130° C. Special precautions were taken to eliminate errors due to impurities. The degree of dissociation and so called dissociation constants have been calculated for these solutions from 0° to 100° C. These data have been used to calculate a new set of solubility data for calcium hydroxide at temperatures from 0° to 25° C. Solubilities of calcium hydroxide have been measured over this temperature interval by an indirect method, and the results are in fair agreement with the calculated values.

Introduction

As a preliminary to an investigation of the equilibria existing in sulphite cooking liquor (the system CaO-H_2O), the specific conductivity of saturated solutions of calcium hydroxide over the temperature range 0° to 130° C. was required. A survey of the literature revealed that the only previous measurements on conductivities of calcium hydroxide were a series of measurements by Ostwald (9) on unsaturated solutions at 25° C. and measurements by Miller and Witt (7) on saturated solutions at 30° C. The former are admitted by the author to be subject to the experimental error introduced by carbon dioxide contamination. It was decided to measure the specific conductivity of saturated solutions of calcium hydroxide over the entire range from 0° to 130° C., employing a technique ensuring freedom from errors due to contamination by impurities. The data obtained have led to the calculation of a new set of values for the solubility of calcium hydroxide between 0° and 25° C., at which temperatures the previous determinations of the solubility are in very poor agreement with one another.

Apparatus

The cell in which the conductivity measurements were made is shown diagrammatically in Fig. 1. It was made of Pyrex and contained a stirrer S, also made of Pyrex, which was actuated by two electromagnets M_1 and M_2, permitting stirring within the completely enclosed cell. The stirrer was

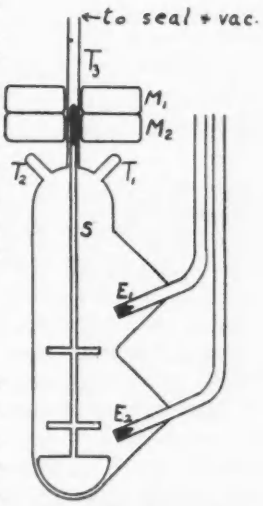

FIG. 1. *Conductivity cell.*

[1] *Manuscript received May 2, 1933.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal Canada.

[2] *Demonstrator, Department of Chemistry, McGill University, at the time of investigation.*
[3] *Holder, at the time, of a studentship under the National Research Council of Canada.*
[4] *Macdonald Professor of Physical Chemistry, McGill University.*

designed to give good agitation, and keep the excess solid in complete suspension. The electrodes E_1 and E_2 were of platinum foil, sealed in the end of Pyrex tubes, which in turn were sealed into "bay windows" in the side of the cell. The electrode assembly as well as the other features of the cell were all designed with a view to preventing solid from depositing in places where it would not be subject to the action of the stirrer. The side arm, T_1, when opened, was used to introduce calcium oxide. Water was distilled into the cell through T_2. T_3 served as a guide for the stirrer and also led to the vacuum pump; it could be closed by means of a mercury seal.

The cell was immersed in a constant-temperature bath in which water was used at low temperatures and oil at high temperatures. To prevent condensation of water in the exposed portion of the tube T_3, it was wound with resistance wire, which could be electrically heated, and covered with asbestos, in order that the temperature of the tube could be kept above that of the bath.

The electrodes were platinized and the cell constant determined in the usual way. There was a small lead resistance due to the thinness of the platinum foil of the electrodes and the leads to the bridge. This was measured by short-circuiting the electrodes with mercury and measuring the cell resistance under these conditions.

In making all resistance measurements a Leeds and Northrup helical slide wire was used. It, as well as the resistance box, had been previously checked and found satisfactory. A Vreeland oscillator, operating at a frequency of 1000 cycles, supplied the current. The null point was detected by means of ear phones.

Materials

Calcium oxide was prepared from Iceland spar by heating the ground crystals in a furnace at 100° C. for several days. It was tested for freedom from carbon dioxide in two ways: first, by dissolving a sample in acid and bubbling any gas produced into barium hydroxide; second, by covering a small lump with gelatin and allowing acid to diffuse through the gelatin and react with the lime—any carbon dioxide liberated was trapped beneath the gelatin and could be seen as a bubble, with aid of a microscope. No carbon dioxide was found by either of these methods. Distilled water was freed of dissolved gases by a series of cycles of freezing (in carbon dioxide snow), evacuating, and melting. It was then slowly distilled into the cell at its own vapor pressure, through the side arm T_2, which was then sealed off.

Procedure

Lime was placed in the cell in considerable excess of the amount needed for saturation. Water was distilled into the cell, and the solution was stirred until equilibrium was reached, as shown by constancy of the specific conductivity during at least 30 min.; but since equilibrium was reached very slowly it was very difficult to use this method at the higher temperatures. At the higher temperatures, the following procedure was adopted: the temperature

of the bath was raised to the desired value and held there during one hour, conductivity readings being taken every 10 or 15 min. The value obtained at the end of an hour was recorded. The temperature was then raised to the next higher value and the procedure repeated. This gave a series of values obtained with ascending temperatures; a similar series was obtained by decreasing the temperature, from the maximum, step by step. The values obtained by these two methods were averaged to obtain an equilibrium value for the conductivity.

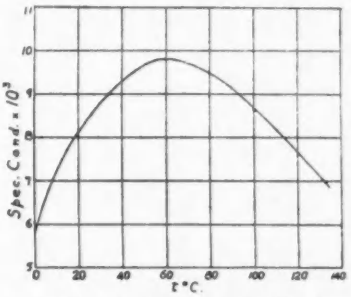

FIG. 2. *Relation between specific conductivity of saturated solutions of calcium hydroxide and temperature.*

The conductivity values are given in Column 2 of Table I. Column 3 contains a set of values for the solubility of calcium hydroxide. These values were obtained from a curve representative of the average of the data of Maben (6), Lamy (4), Herzfeld (3), Guthrie (1), Moody (8), Haslam, Calingaert and Taylor (2) and Miller and Witt (7). Column 4 contains values for the equivalent conductivity at these concentrations. Column 5 contains values for the equivalent conductivity at infinite dilution, calculated from the data of Kohlrausch (5) for the mobility of the ions. Column 6 gives values for the degree of ionization calculated from the equivalent conductivity data. Column 7 gives values for the dissociation constant.

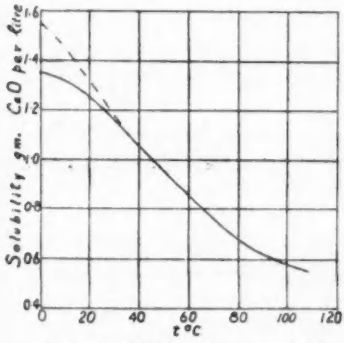

FIG. 3. *Relation between solubility and temperature.*

Owing to the scarcity of solubility data above 100° C., none of the values for solubility, λ_c, λ_o, α, nor K are given above that temperature.

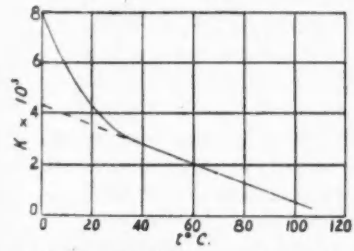

FIG. 4. *Relation between dissociation constant and temperature.*

The values for the specific conductivity of saturated solutions of calcium hydroxide are plotted against temperature in Fig. 2. The average curve for the solubility of calcium hydroxide as obtained from the literature is represented by the continuous line in Fig. 3; the discontinuous portion of this curve will be discussed later. The values of the dissociation constant are plotted against temperature in Fig. 4. The extrapolation of a portion of this curve will be referred to later.

TABLE I

CONDUCTIVITY VALUES AND RELATED CONSTANTS

t°C.	$k \times 10^3$	Solubility of CaO, gm./litre	λ_e	λ_o	α Degree of ionization	$K \times 10^3$
0	5.85	1.351	121.5	145.9	0.832	7.97
10	7.20	1.322	152.7	189.9	0.804	5.89
18	7.99	1.272	176.1	225.0	0.783	4.55
25	8.50	1.207	197.3	255.5	0.772	3.74
37	9.15	1.086	236.3	308.2	0.767	2.91
50	9.66	0.958	283.0	365.2	0.775	2.43
60	9.82	0.860	319.6	409.0	0.781	2.06
70	9.72	0.764	356.3	453.0	0.787	1.70
80	9.48	0.680	390.0	497.0	0.785	1.33
90	9.14	0.620	413.0	540.7	0.764	0.927
100	8.69	0.578	422.0	584.5	0.722	0.576
110	8.20					
120	7.67					
130	7.12					

Discussion

It will be seen in Fig. 4 that the values of the dissociation constant, when plotted against temperature, give a straight line above 37° C.; below 37° C. however the values increase much more rapidly than would be given by a straight line. It was felt that this rather unexpected break in the curve pointed to some inaccuracy in the data used to calculate K, *viz.*, specific conductivities and solubilities.

The specific conductivities appear to be consistent among themselves, and, further, at 30° C., the only point at which other conductivity data are available, the agreement with the value of Miller and Witt (7) is good.

The solubility data used are not so satisfactory. From about 37° to 100° C. the agreement amongst the various determinations is reasonably good, and the values which have been used probably are quite close to the true value. Below 37° C. agreement is not nearly so good, consequently all values in this temperature range must be regarded with some doubt.

Assuming that the values for solubility and, therefore, for dissociation constant, above 37° C. are correct, the dissociation constant-temperature curve from 37° to 100° C. has been extrapolated to 0° (Fig. 4). From these extrapolated values for K, the values have been calculated for the solubility which would be necessary to give such values for the dissociation constant.

These are given in Table II, and are plotted as a discontinuous curve in Fig. 3.

As a check on these calculated solubilities, the solubility has been determined by the following method:

Specific conductivities of unsaturated solutions of calcium hydroxide, of accurately determined concentration, were measured over this temperature interval, the procedure being the same as that used for saturated solutions. The values obtained at a given temperature for a series of solutions of different

TABLE II

CALCULATED SOLUBILITY VALUES

t°C.	$K \times 10^3$ (extrapolated)	$k \times 10^3$	λ_0	Calcd. solubility of CaO, gm./litre
0	4.29	5.85	145.9	1.55
10	3.92	7.20	189.9	1.45
18	3.62	7.99	225.0	1.34
25	3.36	8.56	255.8	1.25

concentration were plotted against concentration. A curve was drawn through these points and extrapolated until it intersected a straight line drawn parallel to the concentration axis and through the conductivity of a saturated solution for that temperature. The concentration at the point of intersection gives the solubility at that temperature.

The conductivity values obtained for these unsaturated solutions are given in Table III.

TABLE III

CONDUCTIVITIES OF UNSATURATED SOLUTIONS

Con'c.: 0.536 gm./litre		Con'c.: 0.737 gm./litre	
t°C.	$k \times 10^3$	t°C.	$k \times 10^3$
2.9	2.60	0.1	3.20
11.9	3.18	10.0	3.99
19.7	3.70	19.7	4.87
30.0	4.31	29.7	5.73

TABLE IV

SOLUBILITY OF CALCIUM OXIDE (gm. per litre)

t°C.	Extrapolation value	Calcd. value	Av. value from literature
0	1.45	1.55	1.35
10	1.39	1.45	1.32
18	1.30	1.34	1.27
25	1.22	1.25	1.21

The two sets of data in Table III, with the origin, give a series of isothermal curves which are slightly concave toward the concentration axis. The solubility values obtained by extrapolating these curves are given in Column 2 of Table IV. In Column 3 the values calculated previously (Table II) are given. The last column gives the average values in the literature.

A comparison of the values in Table IV shows that the calculated values are more nearly correct than the average of the data from the literature, because it seems likely that the values obtained by the straight line extrapolation mark the lower limit of solubilities and that the true values lie between those given by an extrapolation of a curve and by an extrapolation of a straight line, in which case the calculated values must be very nearly correct.

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A POWER LAUNDRY COMPARISON OF THE DETERGENT EFFICIENCIES OF ALKALINE SOAP BUILDERS[1]

By O. M. Morgan[2]

Abstract

Five commonly used alkaline soap builders, namely, caustic soda, soda ash, modified soda, sodium metasilicate, and trisodium phosphate have been tested for detergent efficiency in full-scale power laundry tests. The above sequence represents their decreasing order of efficiency.

Optimum detergent conditions do not occur at the same pH value for each builder nor is the same quantity of soap required to produce effective washing.

All builders studied are free rinsing and produce no loading of the fabrics. Optimum quantities of builder to produce the maximum detergent effect are tabulated.

The problem of comparing different alkalies as soap builders in a full-scale power laundry is one which is beset with many variables and difficulties. Possibly this is the reason why previous experimenters have not put their results on record. One of the main difficulties encountered is the variation in type and intensity of soil on the fabrics to be washed. This soil may be acid or alkaline, usually the former, and the extent of acidity or alkalinity cannot be determined prior to treatment. Its effect on the first suds bath is very marked. In addition to this there occur in the soiled work stains which may or may not be transferable to other fabrics. This is objectionable but unavoidable. Then too there is the personal factor involving the washman. A reliable washman who will carry out his instructions to the letter is of major importance in performing work of this nature.

Through the very kind and whole hearted co-operation of Vail's Laundry, Ottawa, Canada, and Mr. H. G. Vail, facilities were placed at our disposal for the carrying out of the work contained herein. It is not claimed that the results obtained are the last word in this connection. It is felt however that a decided step forward has been made in the study of the actual laundry performance of the common soap builders. No trade preparations have been included in this study. The work has been confined to pure chemicals to which no trade names have been affixed.

Previous Work

In two previous publications (1, 2) the writer has described a method for evaluating and comparing the detergent efficiencies of neutral and built soaps. This work was of a preliminary nature to develop a trustworthy method of making these comparisons and also to determine whether different detergent effects existed. Preliminary figures were obtained as to how pronounced these

[1] *Manuscript received April 7, 1933.*
Contribution from the National Research Laboratories, Ottawa, Canada.

[2] *Assistant Research Chemist, National Research Laboratories, Ottawa.*

differences were. This work was all carried out on laboratory scale. The results indicated that although full-scale experiments in a power laundry would be long and tedious much information could be gained. It was realized however that by carrying out these experiments in a single laundry the results would bear a certain amount of specificity due to local conditions. By this is meant that from one plant to another conditions of soil, water, climate, and general technique would vary. This difficulty unfortunately cannot be conveniently overcome. Since the work is of a comparative nature many of these factors will cancel out giving more weight to the general nature of the results.

Experimental

Test Bundle

The test bundle used in these experiments consisted of a piece of cotton towelling 17 by 18 in. to which was attached a piece of standardly soiled cloth 9 by 9 in. The towelling was used to determine tensile strength losses. It had a thread count of 60–42 and a tensile strength in the filling of 81 lb. per inch. The soiled strip, as in previous work, was used for photometric measurements.

Wash Wheels

Two wash wheels were used. Each of these was constructed with Monel metal cylinders and shells, and wooden ends. The size of the cylinder was 42 in. in diameter and 84 in. in length with four longitudinal ribs 7 in. in height.

These machines were calibrated for volume of water as follows: an average load of soiled clothes and nets, 245 lb., was placed in the cylinder. Successive additions of water were made with an 8-gal. can. At intervals the wheel was allowed to run until an equilibrium water level was reached. It is these equilibrium levels with the wheel in motion that are recorded in Table I.

TABLE I

VOLUME CALIBRATION OF THE MONEL METAL WASH WHEEL (42 BY 84 IN.)

Water level, in.	4	5	6	7	8	10	12	14
Volume, gal.	110	120	129	138	147	164	182	198

It was very important to know the actual volume of water present at any level in order to be able to calculate the amount of soap and builder to use.

Washing Formula

The washing formula used in this work was the recognized "multiple suds" formula. This consists of four suds baths followed by six rinses. The details of this formula are given in Table II.

TABLE II

"MULTIPLE SUDS" WASHING FORMULA

No.	Operation	Water level, in.	Time, min.	Temp., °F.	No.	Operation	Water level, in.	Time, min.	Temp., °F.
1	Break	5	10	100	6	Rinse	8	5	180
2	Suds	4	15	120	7	Rinse	8	5	160
3	Suds	4	15	160	8	Rinse	8	5	130
4	Suds (bleach)	4	15	170	9	Rinse	10	5	100
5	Rinse	4	5	180	10	Blue	12	5	90

Method of Adding Soap

A high quality commercial soap was made up into a 5% liquid soap stock. No builder was added. The analysis of this soap is as follows:—moisture, 2.01; total soap, 97.05; sodium chloride, 0.004; free alkali (as Na_2O), 0.045; glycerol, 0.89%; titer, 39.7° C. The liquid soap was added to the wash wheel in measured quantities.

Method of Adding Alkali and Bleach

The amount of alkali necessary was calculated as a percentage of the weight of water in the wheel. Hence if the amount of water present were 120 gal. and the desired alkali concentration 0.05% the amount of alkali added would be $1200 \times \frac{0.05}{100} = 0.6$ lb.

The alkalies were weighed out into bottles and added to the wash wheel in the dry form prior to adding the soap. Sufficient water was added to the wash wheel to bring it to the desired level before the alkali addition was made. In the case of caustic soda the material was dissolved in a small amount of water and added to the wash wheel very slowly. The same amount of alkali was added to each suds bath. A slightly greater amount was used in the "break" operation due to the higher water level, all concentrations being in weight percentage of the water present. It is realized that the builder additions to the last two suds baths are larger than those commonly found in plant practice. The reason for maintaining the same concentration throughout the sudsing operations was to facilitate obtaining comparative results.

Two quarts of sodium hypochlorite bleach carrying 1.0% available chlorine per 100 lb. of clothes was added in the fourth operation.

Washroom Control

The off wash liquors from each operation in five consecutive washes were titrated against 0.1 *N* nitric acid using both methyl orange and phenolphthalein as indicators. pH determinations were also made using a Taylor long range slide comparator. This instrument was previously checked against electrometric pH measurements on buffer solutions covering the laundry pH range. In this way a careful check was kept on the uniformity of the washing. Data were also obtained on the free rinsing qualities of the various builders and were further substantiated by subsequent ash determinations on the test pieces. This will be discussed in a later section.

Photometric Measurements

After 2, 5, 10, and 20 washes photometric measurements were conducted on the standardly soiled strips using a Zeiss Pulfrich photometer. The increase in brightness of the fabrics is considered as the criterion of washing efficiency.

Tensile Strength Measurements

After the completion of 20 washes tensile strength measurements were made using an Alfred Suter tensile strength machine having breaking ranges of 0–150 and 0–300 lb. Tensile strength losses are given in a later section.

Results

In laboratory experiments previously recorded (2) optimum concentrations of soap builders were determined at which maximum washing efficiency was obtained. In the present experiments concentrations of builder both above and below these optimum concentrations were tried out. The concentrations of builder used are given in Table III in weight percentage.

TABLE III

CONCENTRATION OF BUILDER IN WEIGHT %

Conc. No.	Soda ash	Trisodium phosphate	Modified soda	Sodium metasilicate	Caustic soda
1	0.013	0.03	0.01	0.026	0.004
2	0.026	0.06	0.05	0.052	0.008
3	0.053	0.12	0.10	0.104	0.020
4	0.106	0.24	0.20	0.208	0.040

In each case it was at concentration No. 2 that maximum efficiency was obtained in the laboratory experiments. In Fig. 1, where increasing brightness is plotted against number of washes, it will be noted that concentration No. 2 is again predominant with respect to efficiency in the plant experiments. This may not be the exact concentration for maximum efficiency

but approximates it quite closely. This contention is maintained for two reasons. In the first place laboratory and plant concentrations check for the optimum value. In the second place a manufacturer of sodium metasilicate advises the use of 0.33 lb. of this product per 100 lb. of clothes being washed. This value has been obtained by practical experience in the plant and by laboratory test. The amount of metasilicate recommended by the results obtained in this work is 0.27 lb. per 100 lb. of clothes. These values may be considered to be in good agreement when all variables are considered.

From Fig. 1 it is apparent that in the cases of caustic soda, sodium metasilicate, and modified soda, concentration No. 2 is definitely more efficient than the other concentrations used. In the case of trisodium phosphate (indicated as T.S.P.) concentration No. 2 leads the field after 10 and 20 washes which is quite definite proof of its superiority. In the case of soda ash the differences in efficiency are not so pronounced from one concentration to another. Repeated experiments gave similar results. However at the end of 2, 5 and 10 washes concentration No. 2 shows a slight superiority. This slight difference in efficiency at various concentrations for soda ash also showed up in previous work (2) where it was noted that an efficiency peak existed which was not sharp or well defined. In contrast to this, caustic soda exhibited a very sharp and well-defined efficiency peak. In the present work (see Fig. 1) caustic soda shows decided optimum conditions to exist at concentration No. 2, which was the peak concentration in the previous work.

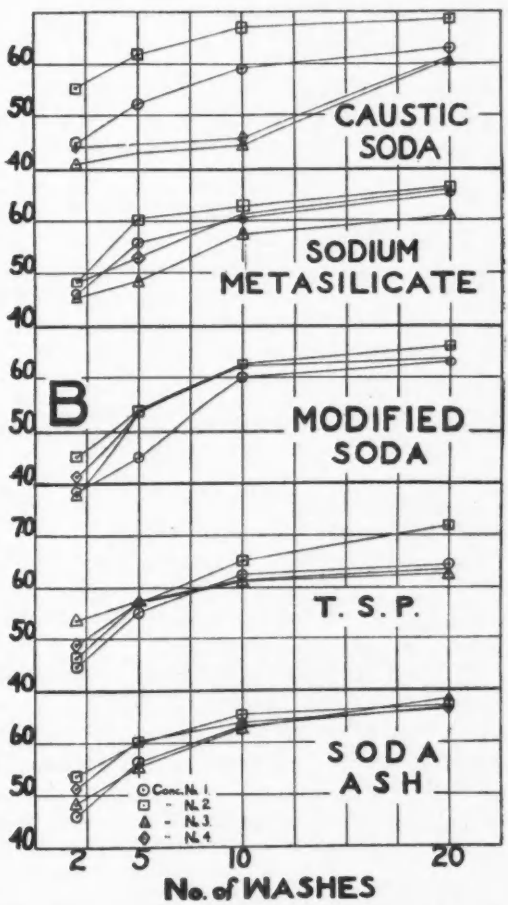

FIG. 1. *Increasing brightness of soiled cloth plotted against number of washes.*

In Fig. 2 increasing brightness is again plotted against number of washes and the curves of concentration No. 2 for each of the five alkalies are compared for relative efficiency. It will be noted that smooth and nearly parallel curves exist for caustic soda, soda ash, and modified soda, falling in the foregoing order of decreasing efficiency. The curves for trisodium phosphate and sodium metasilicate intersect at certain points. This makes exact comparisons uncertain on some aspects of the case. The broad conclusions regarding these builders are however unaffected.

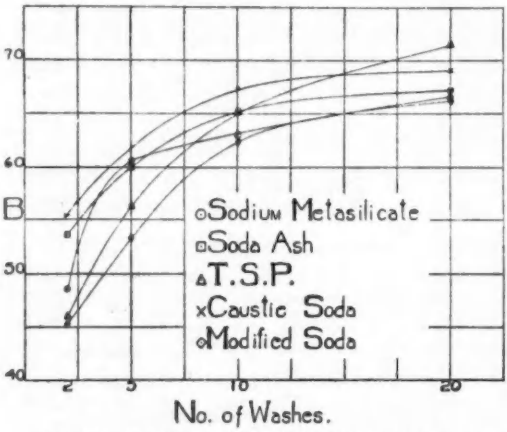

FIG. 2. *Relative builder efficiencies compared under optimum conditions.*

At this point the following question may be raised: "After how many washes is it practical to make efficiency comparisons when the comparisons are based on test bundle results?" From the experience gained in this work it has been found that after 2 or 5 washes the results are based to too great an extent on the idiosyncrasies of the individual washes. After 5 washes individual factors begin to disappear and more definite conclusions may be drawn from the 10- and 20-wash data.

After visiting approximately 100 laundries both in Canada and the United States the writer has been impressed by the fact that equally good grades of finished laundered fabrics are being turned out with various combinations of supplies, provided that certain important features of technique are observed. These may be summarized as follows:

(*a*) The maintenance of a high suds on the "break" operation.

(*b*) The maintenance of a good running suds on the succeeding sudsing operations. Poor quality work is often the result of allowing a suds to fall before the operation is complete.

(*c*) The maintenance and proper use of a stock soap solution that is properly blended with respect to soap and alkali.

(*d*) Careful temperature control and adequate rinsing facilitated by an ample hot water supply is very important. Water of zero hardness should be used.

In Fig. 2 where optimum conditions of the five alkalies are compared it will be noted that after 10 and 20 washes the difference in efficiencies is not very pronounced, nor did the quality of the actual washing in the plant itself vary to any marked extent. Hence comparisons of the efficiencies of these builders cannot be logically made from a quality standpoint. The proper

concentrations of builder to be used must be stressed. A comparison of these concentrations combined with the amount of soap necessary to produce effective washing gives the clearest picture of the situation.

Considering for the moment only actual washing efficiency with a given fixed concentration of soap and optimum conditions as regards concentration of builder, an equal efficiency figure will be ascribed to each builder. Let it be the average brightness figure for 10 washes, which is approximately 65. In Table IV comparative figures for the five builders are presented.

TABLE IV

EFFICIENCY DATA FOR ALKALINE SOAP BUILDERS

Alkali	Efficiency	Alkali conc., %	Alkali efficiency index	Pound efficiency index
Caustic soda	65	0.008	8125	1
Soda ash	65	0.026	2500	3.2
Sodium metasilicate	65	0.052	1250	6.5
Trisodium phosphate	65	0.06	1083	7.5
Modified soda	65	0.05	1300	6.2

Table IV is practically self explanatory. The alkali concentration given is that for maximum efficiency. The alkali efficiency index is obtained by dividing the arbitrary efficiency value of 65 by the alkali concentration. Hence the alkali efficiency indices compare the relative efficiencies per unit weight of builder. This is expressed in a different manner in column No. 5 where pound efficiency indices are given. The number of pounds of other builders that will do the same work as one pound of caustic soda are listed. In order of decreasing efficiency they are caustic soda, soda ash, modified soda, sodium metasilicate, and trisodium phosphate.

Another factor which must not be neglected is the amount of soap to be used with each of these builders to produce adequate lathering. In Table V the amount of soap used in washing 225-lb. loads of very dirty white work in a 42 by 84 in. wash wheel using a 5-in. water level is given. A high suds was maintained on the break operation and a good running suds on the following operations.

From Table V it is readily seen that caustic soda particularly and also sodium metasilicate do not require as much soap as the other builders studied to produce good washing. This will further modify their efficiency indices given in Table IV.

Since the amount of soap used to wash a given quantity of soiled fabrics will vary, depending on

TABLE V

SOAP CONSUMPTION WITH VARIOUS ALKALIES

Alkali	Pounds of soap to wash 225 lb. of clothes
Caustic soda	2.6
Soda ash	4.0
Sodium metasilicate	3.4
Trisodium phosphate	4.0
Modified soda	4.2

local conditions, it is not proposed to advocate any definite soap allotment. However, some data on the quantities of alkali to use are very important. From the experience gained in the present work it is felt that a liquid soap stock to which alkali has been added is not in the interests of economy. It has been shown herein that definite concentrations of alkali produce a maximum detergent effect when sufficient soap is present to maintain a suds. Further additions of alkali are wasted. When alkali and soap are mixed in a built soap stock one cannot be used without the other. Hence it is recommended to maintain a neutral liquid soap stock and add the builder either dry or in solution. In the case of caustic soda it is very essential that the alkali be added to the wash wheel in solution.

In Table VI the quantities of alkali found to produce optimum results in the present work are listed. Slight tolerances are allowable but must not exceed 2 or 3%. Sufficient soap was added to produce a high suds on the break and a running suds thereafter.

TABLE VI

ALKALI ADDITIONS FOR OPTIMUM RESULTS

Operation	Caustic soda, lb.	Soda ash, lb.	Sodium metasilicate, lb.	Trisodium phosphate, lb.	Modified soda, lb.
Break	0.10	0.30	0.62	0.72	0.60
Suds	0.09	0.25	0.55	0.60	0.55

Discussion of Results

Caustic Soda

In the present work caustic soda exhibited the highest detergent efficiency per unit weight. Several points in connection with its use cannot be too strongly stressed. Primarily the concentration range within which it exhibits its maximum effect is very narrow. Hence too great care cannot be taken in order that the proper amounts may be used. If these amounts are too great or too small faulty work will be the result. Care should be exercised in handling this substance. Solutions should always be prepared using cold water since much heat is evolved during the process of solution.

pH Values for Maximum Detergency

The pH values at which maximum detergent effects were noted varied considerably. For soda ash, trisodium phosphate, and modified soda the maximum pH values obtained during the sudsing operations were 10.1–10.2. Sodium metasilicate gave optimum results at a pH value of 10.8 and caustic soda at 10.6. These values are all lower than those obtained in the laboratory (2) and are at variance with the laboratory results of Rhodes and Bascom (3). The lowering of the pH values may be attributed to the residual acidity in the soiled fabrics as well as a slight hardness in the water used.

Free Rinsing Properties and Loading of the Fabrics

It is sufficient to say that no trouble was experienced in rinsing out any of the alkalies used in this work. Titration data combined with ash determinations on the fabrics after 20 washes conclusively proved this point. When a multiple rinse formula is used and an adequate supply of hot water is available no fears in this direction need be entertained.

Tensile Strength Losses

The test fabrics used in these experiments showed quite normal tensile strength losses after 20 washes in the majority of cases. The results are given in Table VII.

TABLE VII

TENSILE STRENGTH LOSSES

Alkali	Soda ash	Trisodium phosphate	Modified soda	Sodium metasilicate	Caustic soda
Tensile strength loss, %	10.7	8.0	8.5	12.2	11.4

The loss of 12.2% incurred with the use of sodium metasilicate is questionable. Other laundries using sodium metasilicate report tensile strength losses in the region of 10.5%. So many other factors blend to give the tensile strength loss that the builder alone cannot be held responsible.

Efficiency Indices

The efficiency indices of the alkalies calculated in Table IV agree remarkably well with those obtained in previous laboratory tests (2). The same order of efficiency was obtained. In the laboratory tests modified soda was not included. This product is third in the order of decreasing efficiency.

Acknowledgments

The writer wishes to express his appreciation to Mr. H. G. Vail and staff of Vail's Laundry, Ottawa, for their assistance in these tests; to Mr. B. J. Kenalty for his supervision of the power laundry tests; and to Mr. C. W. Davis of these laboratories for his analyses of the alkalies used.

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THE ALKALOIDS OF FUMARACEOUS PLANTS

VII. *Dicentra eximia* (KER) TORR.[1]

By R. H. F. Manske[2]

Abstract

A chemical examination of *Dicentra eximia* has resulted in the isolation of six alkaloids. Protopine and dicentrine together constitute the greater portion of the total bases while *d*-glaucine was obtained in minute amounts. Two of the three other alkaloids, all of which appear to be new, resemble corydine and isocorydine and have been named *eximine* and *eximidine* respectively. They are isomeric and are best represented by the formula, $C_{17}H_{13}N(OMe)_2(OH)$. The sixth base was obtained in traces only and until further characterized will be referred to as alkaloid (δ). The yields of purified alkaloids obtained were as follows: dicentrine, 0·41; glaucine, 0·03; eximine, 0·30; eximidine, 0·04; protopine, 0·45; alkaloid (δ), 0·01%: total, 1·24%.

The alkaloid isolated by Eggleston, Black and Kelly from *D. eximia* and named *eximine* by them is identical with dicentrine.

Only three species of *Dicentra* are native to eastern North America and of these *D. canadensis* and *D. cucullaria* formed the subject of the first two papers of this series (4, 5). In continuation of a program of research previously outlined and in order to render the investigations sufficiently comprehensive it was deemed essential to include the third representative, namely, *D. eximia*. This attractive plant is native to the eastern United States growing quite abundantly in southwestern Virginia from which locality the greater part of the material used in the present investigation was obtained. In Virginia and probably elsewhere it is known by the appropriate name of wild bleeding heart. It has been introduced into cultivation for ornamental purposes and is adequately described botanically by Eggleston, Black, and Kelly (1).

The only chemical examination on record is one by the above authors (1), who reported the isolation of a crystalline base, eximine, melting at 165° C. (? corr.) together with amorphous bases. Eximine was stated to yield a hydrochloride of exceptionally slight solubility in cold water—a property which rendered its isolation particularly facile, and no difficulty was encountered in isolating the same base in the course of the present investigation.

Aside from this base, protopine and *d*-glaucine together with three new bases, all phenolic or weakly acidic, were obtained in the present work.

The *eximine* of Eggleston and coworkers was found to melt at 169° C.* and yielded on analysis figures which point unmistakably to the empirical formula $C_{20}H_{21}O_4N$. The methiodide and the derived methine base are normal and confirm the formula. Phenolic hydroxyls are absent and a Zeisel determination indicates the presence of two methoxyl groups. Finally, Hoffmann degradation yields trimethylamine in two stages so that an N-methyl group is functional.

[1] *Manuscript received March 28, 1933.*
Contribution from the National Research Laboratories, Ottawa, Canada.

[2] *Associate Research Chemist, National Research Laboratories, Ottawa.*

* *All melting points are corrected.*

Dicentrine is the only known alkaloid which possesses all of these properties. On some points, however, the literature is either vague or incomplete and for the opportunity of an exact comparison the author is greatly indebted to Dr. R. D. Haworth, formerly of Oxford Univeristy, who supplied a liberal specimen of authentic *d*-dicentrine. Although the latter had discolored slightly it still melted at 165° C. and admixture with the base from *D. eximia* showed no depression. The picrates from both sources, either alone or admixed, melted at 180° C. Since a remote possibility of non-identity still existed further comparison seemed desirable, and no derivative more suitable than the methine base could have been chosen. Not only is it obtainable in quantitative yield, but it crystallizes with great facility. Alone or admixed, the methines from both sources melted at 159° C. The name eximine for this base is therefore to be deleted from the literature.

In view of the great morphological similarity of *D. eximia* and D. *formosa* it is not surprising that dicentrine should be a common constituent.

The isolation of the remaining alkaloids, adequate details of which are given in the experimental section, was accomplished by a procedure which was partly developed in the case of *D. canadensis* (4) and somewhat elaborated and more specifically described in a communication treating of *Adlumia fungosa* (6). Well over 95% of the total basic fraction has been obtained in pure crystalline form, and efforts to isolate pure individuals from the small residuum are in progress.

Protopine, that universal constituent of Fumaraceous plants, was obtained in considerable quantity and in a high degree of purity.

Associated with dicentrine in the non-phenolic bases the hydrochlorides of which are removed from aqueous solution by means of chloroform (Fraction —BC) (6) a small amount of *d*-glaucine was found. It is pertinent to note that the latter has been isolated hitherto only from *Glaucium luteum (flavum).** Glaucine differs from dicentrine only by the substitution of two methoxyls for one methylenedioxy group, and it is of interest to learn of another example of a plant which is capable of effecting the two types of etherification on the one phenolic precursor. The relative proportion of the two types of ethers is perhaps an indication that methylenation is the more facile of the two processes when one of the hydroxyls is in a sterically hindered position. The widespread occurrence of protopine and the occasional though meagre copresence of cryptopine may be regarded as a similar case.

One of the three presumably new alkaloids was obtained in excessively minute amounts. It has been obtained in a crystalline condition only in the form of salts, and further characterization has been delayed until more material is available. It resembles bicucine (7), in that it is soluble in an excess of aqueous ammonia as well as in fixed alkali, but does not appear to be identical with it. It will be referred to as alkaloid δ.

The remaining two alkaloids to which it is proposed to assign the names *eximine*† and *eximidine* are phenolic and both are removable from alkaline

**The laevo-form has recently been obtained from Corydalis ternata* (3).

†*This term is again available for a new alkaloid in view of the fact that the alkaloid formerly described by this name (vide supra) has been identified with dicentrine.*

solution by means of ether. In this respect they resemble corydine and isocorydine, with which pair they are isomeric, analyses of each yielding figures which are in substantial agreement with the empirical formula, $C_{20}H_{23}O_4N$. The analogy with corydine and isocorydine extends to the presence of one hydroxyl and three methoxyl groups, experiments on the allocation of which are in progress, the assumption being that both alkaloids are aporphine bases.

Separation of eximine and eximidine was effected by fractional crystallization of the hydrobromides from water, eximine hydrobromide being only very sparingly soluble. Eximine, like corydine, crystallizes with methanol of crystallization, which is retained very tenaciously. The crystals obtained by adding ether to a concentrated methanolic solution retain one molecule of the latter solvent and then melt at 117° C. When recrystallized from pure ethyl acetate no solvent of crystallization is retained and the alkaloid then melts at 142° C.

Eximidine was obtained in lesser amounts than its isomer. It melts at 133° C. and does not appear to retain solvent of crystallization with any tenacity.

The above record applies only to the roots and underground portion of the plant. The investigation of the aerial portion is in progress.

Experimental

The designations used in the following section refer to the fractions obtained in a manner precisely analogous to the procedure outlined in the case of *Adlumia fungosa* (6).

Isolation of Dicentrine

The methanolic extract (E) after removal of solvent, yielded after two extractions with dilute hydrochloric acid the residue (R) and the aqueous solution (S). Owing to the very sparing solubility of dicentrine hydrochloride in cold water the dark residue (R) contained a large amount of this salt. It was partly removed by repeated extraction with hot water and filtration through a layer of charcoal. The combined extracts were evaporated somewhat and the hydrochloride which separated on cooling was filtered off. The filtrate was added to (S).

The insoluble residue retained dicentrine very tenaciously and to recover the remainder, the mixture which had become contaminated with charcoal was exhausted in a Soxhlet apparatus first with petroleum ether (which extract proved to be excessively rich in sterols), then with ether (which extract is in process of examination), and finally with methanol. The last extract was poured into boiling dilute hydrochloric acid and the insoluble residue (the examination of which yielded nothing definite) filtered off. The filtrate on cooling deposited a copious yield of dicentrine hydrochloride, the final filtrate from which was combined with (S). To the latter solution there was also added the mother liquor from a recrystallization of all of the dicentrine hydrochloride obtained as described above.

The solution (S) was clarified by means of a little charcoal and exhausted with chloroform (C). The non-phenolic base (BC) obtained from this was converted to hydrochloride and the dicentrine salt crystallized as completely as possible by working up the mother liquors.

There was thus obtained a second lot of dicentrine hydrochloride which was combined with the first, and the entire product converted into free base by treatment in hot aqueous solution with potassium hydroxide. The base which became granular and crystalline in several days was filtered off and washed with water. After drying at 65° C. it was dissolved in a large volume of methanol, filtered with the aid of charcoal, and evaporated somewhat. On cooling pale yellow stout prisms of dicentrine, melting at 168° C. were obtained. After two more recrystallizations from the same solvent the crystals were brilliantly colorless and melted constantly at 169° C. When admixed with an authentic specimen of *d*-dicentrine melting at 165° the melting point was not quite sharp at about 167° C. Calcd. for $C_{20}H_{21}O_4N$: C, 70.80; H, 6.20; N, 4.13; 2 OMe, 18.20%. Found: C, 70.75; H, 6.27; N, 4.38; OMe, 18.45%.

The picrates of both specimens were prepared side by side in hot methanolic solution. After one recrystallization, from the same solvent and washing with ether, the picrates melted at 180° C. either alone or admixed.

Dicentrine Methine

The methiodide of dicentrine when recrystallized from water is stated to retain a molecule of water of crystallization and then melt at 224° C. It has now been found that it is more conveniently recrystallized from methanol, particularly if a little ether is added, and then retains one molecule of methanol of crystallization. As thus obtained the substance melts at 188-189° C. Calcd. for $C_{20}H_{21}O_4N.CH_3I.CH_3OH$; N, 2.73; I, 24.75%. Found: N, 2.87; I, 24.06%.

For the preparation of the methine base it is not necessary or desirable to purify the methiodide. Furthermore, dicentrine of almost any quality as long as it is crystalline will suffice. The free base is dissolved in a mixture of chloroform and methanol and heated under reflux for about one hour with an excess of methyl iodide. The solvent is then distilled off, the residue dissolved in hot water, filtered from a slight turbidity and the cooled filtrate basified with an excess of potassium hydroxide. When impure dicentrine has been used, a turbidity may be produced at this point. In order to remove this, and as a general precaution it is desirable to filter the alkaline solution again with the aid of charcoal. The brilliantly clear and generally colorless filtrate is then heated on a steam bath. In a short while a slight turbidity develops, and this is shortly replaced by brilliant colorless flat plates which are filtered off after several hours of heating. As thus prepared the thoroughly washed and dried *dicentrine methine* melts sharply at 158-159° C. When recrystallized from methanol in which it is only sparingly soluble when cold it melts at 159° C. A dilute alcoholic solution displays a very intense bluish-violet fluorescence.

The methine prepared from a specimen of *d*-dicentrine supplied by Dr. R. D. Haworth exhibited identical properties. Calcd. for $C_{21}H_{23}O_4N$; C, 71.39; H, 6.52%. Found: C, 71.61; H, 6.94%.

Dicentrine methine hydrochloride was recrystallized from hot water and then consisted of colorless needles which are only sparingly soluble in cold water or methanol. When heated in a melting point tube there is no appreciable color change until a temperature of 302° C. is reached when melting and effervescence take place.

The methine methiodide was prepared by treatment with an excess of methyl iodide in methanol-chloroform. After removal of the solvents the residue was recrystallized from a large volume of hot water in which it is only sparingly soluble. It was obtained in very pale yellow fine prisms. When heated with excess potassium hydroxide in aqueous solution, trimethylamine is given off and a partly crystalline deposit is obtained. This polymerized somewhat when attempts to recrystallize it were made. It is evidently a substituted phenanthryl-ethylene.

Isolation of Glaucine

The aqueous mother liquor from the dicentrine hydrochloride obtained from (BC) (p. 595) was basified with excess potassium hydroxide, and the liberated base extracted with a large volume of ether. The ether solution was repeatedly washed, first with aqueous potassium hydroxide and then with water. It was then dried over potassium carbonate and the solvent partly distilled off. The concentrated solution deposited a small amount of protopine in the course of several days. This was removed and the base in the mother liquor converted to hydrochloride again. In the course of several days a small amount of dicentrine hydrochloride crystallized out. This was filtered off and the base again regenerated from the mother liquor. Extraction of the basified solution with ether as before and evaporation of the solvent yielded a pale yellow resin which in this condition failed to crystallize. It was therefore completely freed of ether and the residue repeatedly extracted with boiling petroleum ether (50-60° C.). An insignificant amount of dark tarry insoluble material was discarded. The combined extract was evaporated to a small volume when a further small amount of dark resin separated. This was again removed and the resulting pale yellow solution evaporated until a second viscous liquid phase separated. Sufficient highly purified ether to redissolve the latter was added and the solution set aside in a warm place in a stoppered flask. In the course of several days a crust of pale yellow crystals had separated. After removal of the mother liquor the solid (m.p., 117-119° C.) was washed cautiously with ether and recrystallized from the same solvent. As thus obtained the *glaucine* consisted of very pale yellow prisms melting sharply at 120° C. It dissolved in cold sulphuric acid to a colorless solution which slowly became blue. When the solution was heated an intense violet or purple coloration was developed which changed to orange on dilution with water. Calcd. for $C_{21}H_{25}O_4N$; C, 70.99; H, 7.04; 4 OMe, 34.93%.

Found: C, 71.17; H, 7.11; OMe, 34.76%. The base was further identified as glaucine by comparison with an authentic specimen which, after recrystallization from hexane, melted sharply at 120° C. A mixture of the bases from the two sources melted at the same temperature. The author is greatly indebted to Prof. G. Barger of the University of Edinburgh for the specimen of glaucine which was prepared from boldine.

The non-phenolic aporphines are characterized by the readiness with which they react with alkyl chloro-formates in the presence of alkali to yield N-carbethoxy derivatives of β-methylaminoethyl-phenanthrenes (2, 8). The latter are for the greater part well crystallized compounds and may serve for the purpose of characterization.

Since the substance from glaucine does not appear to have been described its preparation was effected by the method of Osada (8).

N-Carbethoxy-8-(β-methylaminoethyl)-2, 3, 5, 6–tetramethoxy-phanthrene was obtained in large colorless rhombic plates sparingly soluble in cold methanol or ether, but very soluble in chloroform; m.p., 115° C. Calcd. for $C_{20}H_{29}O_6N$; N, 3.28%. Found: N, 3.27%.

Isolation of Eximine

The fraction (EC) (namely, the bases whose hydrochlorides are extracted from an acid aqueous solution with chloroform and which are removed from solution in excess fixed alkali by means of ether) was treated in methanol with an excess of concentrated hydrobromic acid. Crystallization was almost immediate and practically complete. The hydrobromides were filtered off, washed with cold methanol and recrystallized twice from hot water. The least soluble fraction then had the appearance of homogeneity.

Eximine hydrobromide as thus obtained consists of colorless equilateral deep rhombic plates which when rapidly heated begin to darken at 248° C. and melt with decomposition at 270° C.

The free base is conveniently obtained from the hydrobromide as follows. The salt is dissolved in hot water and the clear solution cautiously treated with dilute ammonia solution until the incipient turbidity is just permanent. In a short time the free base crystallizes and the addition of ammonia is then cautiously continued until an excess is present. The mixture is allowed to remain overnight in an ice chest and the crystals filtered off, and washed with cold water. After drying in an oven at 65° C. the base as thus obtained melts at 142-143° C.

Eximine is best recrystallized from purified ethyl acetate, in which it is moderately soluble, and then consists of stout quadrangular prisms with oblique terminations. When this product is thoroughly dried it melts at 142° C. Calcd. for $C_{20}H_{23}O_4N$; C, 70.36; H, 6.75; N, 4.13; 3 OMe, 27.27%. Found: C, 69.58; H, 6.95; N, 4.48; OMe, 27.25%.

Eximine may also be readily recrystallized by adding dry ether to a concentrated methanolic solution. Long stout needles are thus obtained which melt not quite sharply at 116-117° C. with the evolution of a gas, probably

methanol. When this substance was dried overnight in a high vacuum over phosphorus pentoxide and then dried to constant weight at 100° C. it lost 5.5% of its weight. It is therefore probable that in the freshly crystallized substance one molecule of methanol (8.6%) is present, part of which was lost in the high vacuum. This behavior is strictly analogous to that of corydine.

Eximine methiodide was prepared by treating a chloroform-methanol solution of the base with excess methyl iodide. After 24 hr. the solvent was removed, the residue dissolved in water and the filtered solution (charcoal) evaporated to a syrup. The addition of a little methanol and then ether yielded colorless elongated prisms sparingly soluble in cold methanol. When heated, solvent of crystallization was lost at about 180° C. at which temperature slight darkening took place. At 212° C. melting with charring and effervescence took place. Analyses are in agreement with the dihydrate. Calcd. for $C_{20}H_{23}O_4N.CH_3I.2H_2O$; N, 2.70; I, 24.47%. Found: N, 2.70; I, 24.95%.

Isolation of Eximidine

The methanolic mother liquor from the first crystallization of eximine hydrobromide was freed of solvent and the residue dissolved in hot water. Excess potassium hydroxide was added to the filtered solution (charcoal). A small amount of protopine was precipitated. The filtrate from this was saturated with ammonium chloride and extracted with ether. The extract was evaporated to a small volume and a turbidity removed by filtration with charcoal. The filtrate on further evaporation rapidly deposited fine colorless needles which were filtered off and washed with cold ether in which the base is sparingly soluble. It was recrystallized by dissolving in a little acetone, evaporating to a resin and adding a large volume of ether. A slight turbidity was removed with the aid of charcoal and the filtrate rapidly evaporated. Long colorless needles of *eximidine* were thus obtained which melted sharply at 133° C. Calcd. for $C_{20}H_{23}O_4N$; C, 70.36; H, 6.75; N, 4.13; 3 OMe, 27.27%. Found: C, 69.42; H, 6.73; N, 4.26; OMe, 27.00%.

Eximidine methiodide prepared in the usual way proved to be very difficult to purify. After many charcoal treatments a methanol solution was treated with ether and the turbidity rapidly filtered off. The filtrate then deposited colorless slender needles which after filtering off were washed with ethyl acetate and with ether. They began to darken at 190-195° C. and frothed to a black mass at 218° C. Calcd. for $C_{20}H_{23}O_4N.CH_3I$; I, 26.29%. Found: I, 25.64%.

Isolation of Protopine

In the writer's experience the plant under discussion offers one of the most convenient sources of protopine. The fraction (AC) when partly freed of chloroform and treated with hot methanol yielded a large quantity of the base which in this condition was only pale brown and melted at 208-209° C.

The mother liquor on appropriate treatment yielded the non-phenolic fraction (BS) which on recrystallization from chloroform-methanol proved to consist almost entirely of pure protopine. The alkaloid was obtained in the

two crystal forms (6) both of which were identical with those from *Adlumia fungosa* and from other sources. No difficulty was encountered in raising the melting point to 211° C. by one or two recrystallizations.

The final mother liquors from the crystallization of the protopine were converted to hydrochlorides. A further amount of protopine as hydrochloride was thus obtained. The mother liquor from this yielded only a few milligrams of amorphous base.

Isolation of Alkaloid δ

The fractions (ES, BSE, and EES) were combined, dissolved in dilute hydrochloric acid and the filtered solution basified with excess potassium hydroxide. A small amount of protopine was precipitated and a further small amount was obtained by extracting the alkaline solution with ether. The alkaline solution was then saturated with carbon dioxide and the precipitated base filtered off and dried. Treatment in methanol with concentrated hydrobromic acid and cautious addition of ether yielded a pale yellow hydrobromide which was recrystallized from methanol by the addition of ether. It was thus obtained in almost colorless fine needles sparingly soluble in cold water. It darkens at 235° C. and melts to a black mass at 239° C. The hydrochloride similarly prepared began to darken at 234° C. and decomposed to a black tar at 237-238° C.

Cautious treatment of an acid solution with ammonia first yields a flocculent precipitate which dissolves in an excess of the reagent.

When a solution of the base in excess of ammonia is freed of the latter in a desiccator over sulphuric acid a semicrystalline crust is obtained. This product is readily soluble in methanol but attempts to obtain the free base in a pure state have thus far failed.

Acknowledgment

The author wishes to express his indebtedness to Dr. Helen Stantiel of Toronto University who kindly submitted some of the analytical figures.

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β-ANTHRONYL-β-PHENYL-PROPIONIC ACID AND ITS DERIVATIVES

SYNTHESIS OF THE γ-ANTHRONYL-α-HYDRINDONE[1]

BY PAUL E. GAGNON[2] AND LUCIEN GRAVEL[3]

Abstract

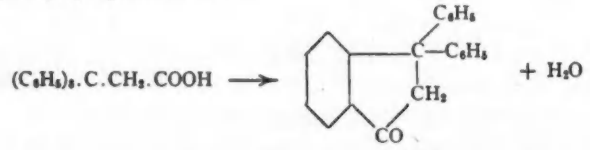
Benzaldehyde and *o*-chlorbenzaldehyde were readily condensed with ethyl and methyl malonate, giving rise to unsaturated esters. The esters were condensed with anthrone in alcoholic solution in the presence of piperidine. Hydrolysis of the product with sulphuric acid yielded β-anthronyl-β-phenyl-propionic acid. The chloride of this acid was formed by the action of phosphorus pentachloride. Two tautomeric derivatives of γ-anthronyl-α-hydrindone result from the action of aluminium chloride on β-anthronyl-β-phenyl-propionyl chloride. No benzanthrone derivatives were formed.

The action of bromine on the two tautomeric forms of γ-anthronyl-α-hydrindone gave rise to one monobromide only, and oxidation of the two tautomers yielded only anthraquinone and phthalic acid.

The method of preparation of β-anthronyl-β-phenylpropionic acid has been improved and the following compounds have been described, as far as the authors are aware, for the first time: the dimethyl and diethyl esters of *o*-chlorbenzylidene-malonic acid and anthrone-*o*-chlorbenzylidene-malonic acid; anthrone-benzylidene-diethyl-malonate; β-anthronyl-β-(*o*-chlorphenyl)-propionic acid; the silver salt, chloride, amide, anilide, methyl and ethyl esters of β-anthronyl-β-phenyl-propionic acid; γ-anthronyl-α-hydrindone (enolic and ketonic forms); γ-anthronyl-β-brom-α-hydrindone; and the hydrazone hydrate, phenylhydrazone, oxime and semicarbazone of γ-anthronyl-α-hydrindone.

Introduction

In recent investigations, one of the writers (2) showed that γ-γ-diphenyl-α-hydrindone (13, p. 1370) can be prepared with good yields by cyclisation of triphenyl-propionic acid.



It was thought interesting to see whether β-anthronyl-β-phenyl-propionic acid, prepared by Meerwein (10, p. 285), would react in the same way and give rise to a new derivative of α-hydrindone (II), or whether, by reacting differently, it would give rise to a derivative of benzanthrone (I).

The main object of the present work was the preparation of β-anthronyl-β-phenyl-propionyl chloride and the study of its cyclisation.

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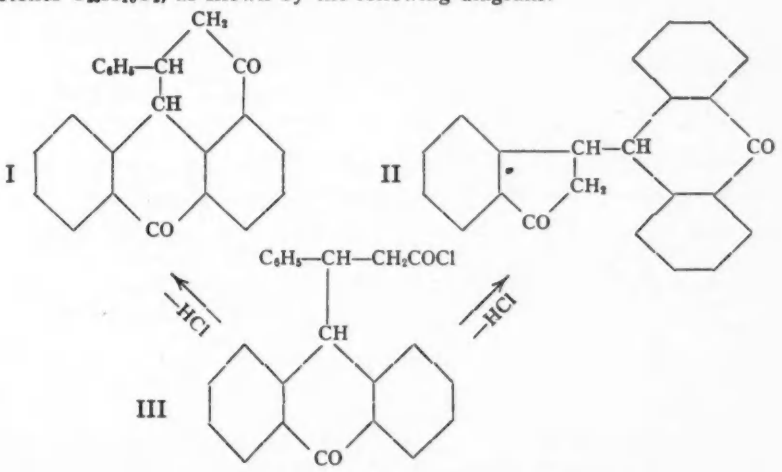
Contribution from the "Ecole Supérieure de Chimie", Laval University, Quebec, with financial assistance from the National Research Council of Canada. This paper is based on a thesis presented by Lucien Gravel in partial fulfilment of the requirements for the degree of D.Sc. at Laval University.

[2] *Professor of Chemistry, Laval University.*
[3] *Graduate Student, Laval University.*

Theoretically β-anthronyl-β-phenyl-propionyl chloride (III), by elimination of one molecule of hydrochloric acid, can form either of the two isomeric ketones $C_{23}H_{16}O_2$, as shown by the following diagram:



Only one of these compounds, (I), was mentioned in the literature; its enolic form has been obtained by elimination of water from β-anthronyl-β-phenyl-propionic acid with sulphuric acid (4, 5, 6).

The writers were not able to obtain it. On the other hand, they did obtain γ-anthronyl-α-hydrindone (II), the two tautomeric forms of which have not hitherto been described. One of the forms melts at 161-162° C. giving a monobromide melting at 170-171°C.; the other melts at 187-188° C. and gives the same monobromide.

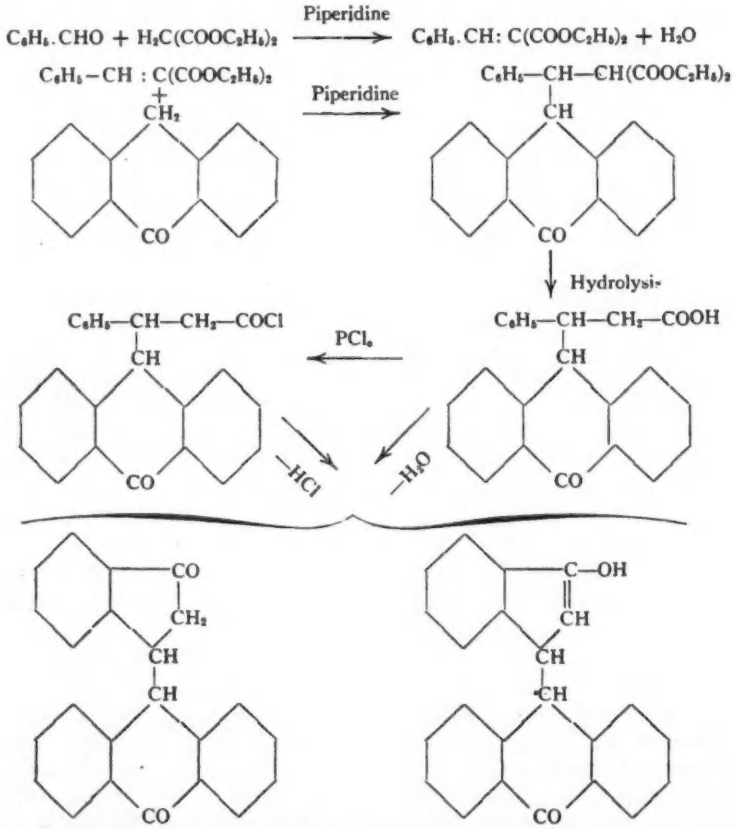
The writers have prepared the two tautomeric forms, by the action of aluminium chloride on the chloride of β-anthronyl-β-phenyl-propionic acid and also from the acid itself by elimination of water with sulphuric acid.

The synthesis was carried out in accordance with the reactions shown on p. 602.

Instead of benzylidene-dimethyl-malonate, used by Meerwein (10, p. 285), benzylidene-diethyl-malonate (7) which is cheaper was employed as the starting material.

Benzylidene-diethyl-malonate was condensed with anthrone and anthrone-benzylidene-diethyl-malonate obtained. By hydrolysis of this ester with sulphuric acid, β-anthronyl-β-phenyl-propionic acid was formed. By treating this acid with phosphorus pentachloride, the chloride was obtained in very good yields. It is a white substance melting at 115-116° C. and not very stable. It was, however, well characterized by preparing many derivatives, and used as starting material for the preparation of γ-anthronyl-α-hydrindone.

In order to establish the constitution of this ketone, the writers determined its molecular weight, and oxidized it by nitric acid according to König's method (8). The only resulting products are anthraquinone and phthalic acid.



This paper deals with: *(a)* the various methods used to obtain β-anthronyl-β-phenyl-propionic acid and β-anthronyl-β-(*o*-chlorphenyl)-propionic acid; *(b)* a study of β-anthronyl-β-phenyl-propionyl chloride and some of its derivatives; and *(c)* a description of the methods of preparation of γ-anthronyl-α-hydrindone, some of its derivatives, and its oxidation products.

Part I

β-Anthronyl-β-phenyl-propionic Acid and β-Anthronyl-β-(*o*-chlorphenyl)-propionic Acid

In this section will be considered: *(a)* the unsaturated esters, benzylidene-diethyl-malonate, and the diethyl and dimethyl esters of *o*-chlorbenzylidene-malonic acid; *(b)* their condensation products with anthrone; and *(c)* the methods used for obtaining β-anthronyl-β-phenyl- and β-anthronyl-β-(*o*-chlorphenyl)-propionic acids.

I. *Unsaturated Esters*

1. *Benzylidene-diethyl-malonate.*—Benzylidene-diethyl-malonate ($C_6H_5.CH : C(COOC_2H_5)_2$) is readily obtained by Knoevenagel's method (7, p. 2591), by condensation of equivalent quantities of benzaldehyde and diethyl-malonate. From 1200 gm. of diethyl-malonate there was obtained 1660 gm. of benzylidene-diethyl-malonate distilling at 184-184.5° C./9 mm. and at 176-177° C./5 mm. Yield, 80%.

2. *o-Chlorbenzylidene-diethyl-malonate.*—*o*-Chlorbenzaldehyde in the presence of piperidine was condensed with diethyl-malonate in a manner similar to benzaldehyde.

The ester formed in this reaction possesses properties very similar to those of benzylidene-diethyl-malonate. It is easily purified, as it distils without decomposition under reduced pressure.

Preparation.—In a 200-cc. conical flask, 50 gm. of diethyl-malonate and 48.75 gm. of *o*-chlorbenzaldehyde were introduced. The mixture was stirred and treated with two grams of piperidine. The well-corked flask was then left at room temperature for 4-5 days. The water formed during the condensation was evaporated off on the water bath.

After cooling, the mixture was extracted with ether and the ethereal solution, washed many times with dilute hydrochloric acid and then with water, was dried over anhydrous sodium sulphate. Ether was distilled off and the sirupy liquid remaining distilled under reduced pressure. Between 178-179° C./4 mm. the distillate was colorless; b.p., 181-182° C./5 mm. The ester was still impure, containing *o*-chlorbenzoic acid which crystallized in small white needles when the distillate was cooled to 0° C. This acid was formed by the oxidation of *o*-chlorbenzaldehyde during the distillation.

To obtain the pure ester the distillate was extracted with ether, the ethereal solution treated with concentrated ammonia, washed many times with water and dried over anhydrous sodium sulphate. The ether was distilled off, and the resulting product redistilled under reduced pressure. The ester then distilled at 182-183° C./5 mm. Yield, 59.6 gm. (theory, 87.7 gm.), *i.e.*, 68%.

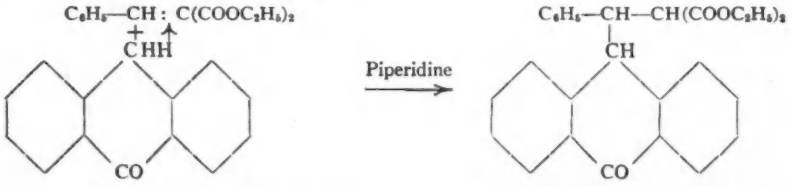
The ester is a colorless liquid having a characteristic odor. On standing it crystallizes, forming colorless prisms; m.p., about 30° C. Analysis:—Calcd. for $C_{14}H_{15}O_4Cl$; Cl, 12.53%. Found: Cl, 12.78, 12.54%.

3. *o-Chlorbenzylidene-dimethyl-malonate.*—Dimethyl-malonate was condensed with *o*-chlorbenzaldehyde as readily as diethyl malonate and the method used was the same. Fifty grams of dimethyl-malonate, 55 gm. of *o*-chlorbenzaldehyde and 2 gm. of piperidine were used. A colorless product was obtained: b.p., 175° C./3 mm. It crystallized on stirring. Yield, 60.6 gm. (63%). The ester is very soluble in most organic solvents, crystallizes readily from petroleum ether and is a colorless substance; m.p. 58-59° C. Analysis: Calcd. for $C_{12}H_{11}O_4Cl$; Cl, 13.93%. Found: Cl, 13.62%.

II. *Products of Condensation of the Unsaturated Esters with Anthrone*

The above-mentioned esters can be condensed with anthrone in the presence of piperidine to form addition products similar to anthrone-benzylidene-dimethyl-malonate prepared by Meerwein (10, p. 285).

The following reaction takes place:—



Anthrone has been prepared by reduction of anthraquinone, dissolved in acetic acid, by means of tin and hydrochloric acid (1, 11, p. 55, 12, p. 8). The anthrone must be free from acetic acid. It was therefore treated with sodium bicarbonate and recrystallized from benzene.

The method of condensation was the same for the three esters.

1. *Anthrone-benzylidene-diethyl-malonate* $C_6H_5.CH(C_{14}H_9O).CH(COOC_2H_5)_2$. This ester was made and used as the starting material for the preparation of β-anthronyl-β-phenyl-propionic acid.

Anthrone (31.3 gm.), crystallized from benzene and free from acetic acid, 43 gm. of benzylidene-diethyl-malonate, 80 cc. of anhydrous methyl alcohol and 30 drops of piperidine were introduced into a 300-cc. flask. A condenser provided with a calcium chloride tube was attached and the flask heated on the water bath. It was very important to shake the flask, to hasten condensation. After 20 min., 20 additional drops of piperidine was added; 10 min. later the anthrone was completely dissolved and the solution had a reddish color. The flask was left on the water bath for another hour.

The solution was rapidly filtered with suction and cooled to 0° C. On stirring the solution, the product crystallized. It was filtered off, and washed with alcohol cooled to 0° C. There was thus obtained 64.5 gm. of a colorless substance melting at 103-104° C. Yield, 90.6%. Recrystallized from methyl alcohol, it melted at 104-105° C.

The ester is soluble in benzene, acetone, chloroform, methyl and ethyl alcohols, ether, and slightly soluble in petroleum ether. Sulphuric acid dissolves it, forming a yellowish solution. Analysis:—Calcd. for $C_{28}H_{26}O_5$: C, 76.00; H, 5.88%. Found: C, 75.96; H, 5.79%.

2. *Anthrone-o-chlorbenzylidene-diethyl-malonate.* Anthrone (27.44 gm.), o-chlorbenzylidene-diethyl-malonate (42 gm.), anhydrous methyl alcohol (25 cc.) and piperidine (25 drops) were introduced into a 300-cc. flask connected with a condenser. After heating on a water bath for an hour the anthrone dissolved. The warm solution was rapidly filtered and cooled; the product crystallizing out. It was filtered off, washed with alcohol and dried. Yield, 72.6%.

Anthrone-*o*-chlorbenzylidene-diethyl-malonate is very soluble in methyl alcohol, but is less soluble in ethyl alcohol. From these solvents it separates in colorless crystals; m.p., 119-120° C. Analysis:—Calcd. for $C_{28}H_{25}O_5Cl$: Cl, 7.43%. Found: Cl, 7.46, 7.57%.

3. *Anthrone-o-chlorbenzylidene-dimethyl-malonate*, $Cl.C_6H_4.CH(C_{14}H_9O)CH(COOCH_3)_2$. This substance was prepared in a manner similar to anthrone-*o*-chlorbenzylidene-diethyl-malonate. The reactants and amounts used were as follows: *o*-chlorbenzylidene-dimethyl-malonate, 21 gm.; anthrone, 15.2 gm.; anhydrous methyl alcohol, 41 cc.; piperidine, 30 drops. Yield, 29 gm. (82.6%). Recrystallized from benzene, which dissolves it readily, anthrone-*o*-chlorbenzylidene-dimethyl-malonate forms colorless prisms melting at 148-149° C. Analysis:—Calcd. for $C_{26}H_{21}O_5Cl$: Cl, 7.93%. Found: Cl, 7.96, 7.97%.

III. *β-Anthronyl-β-phenyl-propionic Acid and β-Anthronyl-β-(o-chlorphenyl)-propionic Acid*

These two acids were prepared by hydrolysis of the malonates just described. The reaction was complete only after heating for four or five days. The speed of the reaction was increased by adding to the hydrolyzing mixture, after boiling for two days, a few crystals of the acid. This caused crystallization of the acid already formed and facilitated the hydrolysis of the remaining ester.

1. *β-Anthronyl-β-phenyl-propionic acid* $C_6H_5.CH(C_{14}H_9O)CH_2COOH$. Two methods of preparation of this acid are known. It was first obtained by Meerwein (10), and more recently (4, 5) by condensation of cinnamic acid with anthrone. The writers used Meerwein's method, employing the diethyl ester instead of the dimethyl ester as the starting material.

Preparation.—Anthrone-benzylidene-diethyl-malonate (210 gm.), 30% sulphuric acid (1500 cc.) and glacial acetic acid (600 cc.) were introduced into a three-litre flask fitted with a rubber stopper and a reflux condenser, and the mixture heated to boiling. The ester melted and separated into small drops which were well stirred by boiling the hydrolyzing mixture. After heating for five days, all the droplets solidified. However, on comparison with a sample of β-anthronyl-β-phenyl-propionic acid, it was observed that the hydrolysis was complete on the fourth day. On seeding, the acid crystallized almost completely; the following day, all the acid had solidified. The contents of the flask was then poured into an equal volume of water. The acid was filtered off, pulverized, washed with water, filtered off and dissolved in a hot saturated solution of sodium bicarbonate. After cooling, the solution of the sodium salt was filtered and acidified with sulphuric acid. The precipitated acid was filtered off and washed with water until free from sulphuric acid. Yield, 135 gm. (82%). The acid obtained by recrystallization from acetic acid and washing with alcohol was white; m.p., 196-197° C. Yield, 102.3 gm. (63%). The residual mother liquor deposited about 9-10 gm. of rather impure acid.

When heated at 100°C. with concentrated sulphuric acid, the acid remains unaltered. It may be distilled under reduced pressure without decomposition. This acid was identified as β-anthronyl-β-phenyl-propionic acid, prepared by Meerwein's method, by a mixed melting point determination.

It was characterized by its silver salt. A paste, made by mixing β-anthronyl-β-phenyl-propionic acid (1 gm., weighed exactly) with a small quantity of water, was dissolved in a few drops of concentrated ammonia and filtered. An excess (0.2-0.4 cc.) of a $N/10$ silver nitrate solution was added to the filtrate with vigorous stirring. The insoluble silver salt separated out immediately in white flakes and was allowed to settle in the dark. The precipitate, washed twice with hot water by decantation, was filtered off, washed again with hot water and dried in the dark over sulphuric acid. Analysis:—Calcd. for $C_{28}H_{17}O_3Ag$: Ag, 24.02%. Found: Ag, 23.91, 23.89%.

2. *β-Anthronyl-β-(o-chlorphenyl)-propionic acid* $Cl.C_6H_4.CH(C_{14}H_9O)CH_2.COOH$.

(a) Preparation from anthrone-o-chlorbenzylidene-diethyl-malonate. Anthrone-*o*-chlorbenzylidene-diethyl-malonate (4 gm.) was treated with 31 cc. of 30% sulphuric acid and 12 cc. of acetic acid. The flask was heated for five days at 130-135° C., and after cooling, the mixture was poured into 200 cc. of water. The insoluble acid was filtered off and dissolved in a hot solution of sodium bicarbonate. The solution was filtered and acidified with dilute sulphuric acid. The precipitated acid was filtered off, washed with water and dried; m.p. 155-156° C. Yield, 2.7 gm.

The acid crystallizes from acetic acid in very small diamond-shaped crystals melting at 159-161° C. It is very soluble in alcohol. Analysis:—Calcd. for $C_{28}H_{17}O_3Cl$; Cl, 9.41%. Found: Cl, 9.47, 9.45%.

(b) Preparation from anthrone-o-chlorbenzylidene-dimethyl-malonate. Anthrone-*o*-chlorbenzylidene-dimethyl-malonate (14.4 gm.) was treated with 40 cc. of acetic acid and 100 cc. of 30% sulphuric acid in a flask fitted with a rubber stopper and a reflux condenser. The mixture was boiled for six days, cooled and poured into water. The insoluble acid was filtered off, washed with water and dissolved in a hot saturated solution of sodium bicarbonate. From this solution, cooled and filtered, the acid was precipitated with dilute sulphuric acid, filtered off and dried at 80° C. Yield, 10.4 gm. M.p. 120° C.

The raw product was easily purified by crystallizing it from acetic acid and washing with ether; m.p. 159-161° C.

This acid was proved identical with that obtained by hydrolysis of anthrone-*o*-chlorbenzylidene-diethyl-malonate by a mixed melting point determination.

Part II

β-Anthronyl-β-phenyl-propionyl Chloride and its Derivatives

In this section will be considered:—*(a)* the two methods for preparing the acid chloride; and *(b)* some derivatives of the acid prepared from the chloride, *i.e.*, esters, amide, anilide, anthrone-benzylidene-acetophenone.

I. *β-Anthronyl-β-phenyl-propionyl-chloride* $C_6H_5.CH(C_{14}H_9O).CH_2.CO.Cl$. The chloride was first prepared with phosphorus trichloride but as resins were also formed, purification of the product was difficult. The pure chloride was obtained in good yields by the action of phosphorus pentachloride.

β-Anthronyl-β-phenyl-propionic acid (30 gm.), phosphorus pentachloride (24.5 gm.) and anhydrous carbon disulphide (180 cc.) were heated to boiling in a 300-cc. flask fitted with a reflux condenser and a calcium chloride tube. The insoluble acid gradually dissolved owing to the formation of the soluble chloride and there was a rapid evolution of hydrochloric acid. The mixture was boiled for about an hour.

After cooling, the solution was rapidly filtered, and the carbon disulphide and phosphorus oxychloride were partly distilled off. Upon cooling and stirring the remaining solution (50-60 cc.) the chloride crystallized; it was filtered off and dried in vacuum. Yield, 31 gm. It was purified by crystallization from anhydrous carbon disulphide. Yield, 28.6 gm. (90.4%). The pure chloride crystallizes from carbon disulphide in colorless diamond-shaped crystals melting at 115-116° C.

The chloride is not a very stable compound. By exposure to air it is slowly transformed into the acid, the same transformation being effected much more rapidly if the chloride is treated with acetic acid. A short boiling with acetic acid transforms it almost quantitatively. The chloride cannot be distilled without decomposition, for even under reduced pressure resins are formed. Analysis:—Calcd. for $C_{23}H_{17}O_2Cl$; Cl, 9.80; C, 76.54, H, 4.75%. Found: Cl, 9.91; C, 76.27; H, 4.67%.

II. *β-Anthronyl-β-phenyl-propionic Acid Derivatives Prepared from the Chloride*

1. *Methyl ester*, $C_6H_5.CH(C_{14}H_9O)CH_2.COOCH_3$. Pure β-anthronyl-β-phenyl-propionic acid (5 gm.), anhydrous benzene (50 cc.) and phosphorus trichloride (5 cc.) were heated together for two hours in a 200-cc. flask fitted with a reflux condenser and a calcium chloride tube. The solution was cooled to room temperature and 80 cc. of methyl alcohol was slowly added. A violent reaction took place, after which the mixture was boiled for 1½ hr. The hot solution was then rapidly filtered, the solvent distilled off and the ester crystallized. It was extracted with benzene, the solution washed with water to eliminate hydrochloric acid, dried with calcium chloride and filtered again; the solvent was partly distilled off and on cooling, the almost colorless ester crystallized.

It was filtered off, dried and recrystallized from methyl alcohol; m.p., 111-112° C. Yield, 4.4 gm. (84.6%). Analysis:—Calcd. for $C_{24}H_{20}O_3$: C, 80.86, H, 5.66%. Found: C, 80.68, 80.67; H, 5.58, 5.51%.

2. *Ethyl ester*, $C_6H_5.CH(C_{14}H_9O)CH_2.COOC_2H_5$. Pure β-anthronyl-β-phenyl-propionic acid (5 gm.), free from water, phosphorus trichloride (5 cc.) and anhydrous benzene (50 cc.) were boiled in a 250-cc. flask fitted with a reflux

condenser and a calcium chloride tube for 2½ hr. After cooling, the solution was filtered and poured into a dry flask; 80 cc. of absolute alcohol was slowly added and the solution boiled for 1½ hr. The solvent was distilled off.

A sirupy product which crystallized finally was left in the flask. The colorless ester was obtained by recrystallization from alcohol; m.p., 88-89° C. Yield, 3.7 gm. (69.5%). Analysis:—Calcd. for $C_{25}H_{22}O_3$: C, 81.04; H, 5.99%. Found: C, 80.93, 80.92; H, 6.00, 5.91%.

3. *Amide*, $C_6H_5.CH(C_{14}H_9O)CH_2.CO.NH_2$. A rapid stream of ammonia was passed through a solution of 7 gm. of β-anthronyl-β-phenyl-propionyl chloride in 25 cc. of anhydrous benzene. After two hours, the solvent had completely evaporated and a crystalline product remained in the flask. It was washed with water and dried at 80° C. Yield, 6.7 gm.

Recrystallized from methyl alcohol, the amide was colorless; m.p., 181-182° C. It is very soluble in benzene and alcohol, and insoluble in petroleum ether. Analysis:—Calcd. for $C_{23}H_{19}O_2N$: N, 4.10%. Found: N, 4.13, 4.10%.

4. *Anilide*, $C_6H_5.CH(C_{14}H_9O)CH_2.CO.NH.C_6H_5$. Two grams of β-anthronyl-β-phenyl-propionyl chloride was dissolved in 20 cc. of anhydrous benzene and 5 cc. of aniline added dropwise to the solution. The anilide immediately precipitated. It was filtered off and washed with water. The product was extracted with ether, and the ethereal solution washed with dilute hydrochloric acid and with water. Ether was distilled off and the remaining product dried. The anilide was purified by recrystallization from alcohol, from which it was deposited in very fine colorless needles. From ether the anilide crystallized in diamond-shaped crystals melting at 168-169° C. Analysis:—Calcd. for $C_{29}H_{23}O_2N$: N, 3.35%. Found: N, 3.36, 3.34%.

5. *Anthrone-benzylidene-acetophenone*, $C_6H_5.CH(C_{14}H_9O)CH_2.CO.C_6H_5$.

By condensation of anthrone with benzylidene-acetophenone, Meerwein (10) obtained anthrone-benzylidene-acetophenone, according to the following reaction:

$$\begin{array}{l} C_6H_5.CH:CH.CO.C_6H_5 \\ \quad + \\ C_{14}H_{10}O \end{array} \xrightarrow{\text{Piperidine}} \begin{array}{l} C_6H_5.CH.CH_2.CO.C_6H_5 \\ \quad | \\ C_{14}H_9O \end{array}$$

The same compound was obtained by the writers by treating β-anthronyl-β-phenyl-propionyl chloride dissolved in benzene with aluminium chloride.

Preparation.—β-Anthronyl-β-phenyl-propionyl chloride (20 gm.) was dissolved in 200 cc. of anhydrous benzene in a three-necked flask fitted with a mercury seal stirrer and reflux condenser and 16 gm. of aluminium chloride was added. A reddish color appeared. The mixture was heated on a water bath at 20° C. for three and a half hours. The temperature was raised till the benzene was boiling, when there was a rapid evolution of hydrochloric acid. After five hours' stirring, the mixture was cooled and poured on broken ice; a small quantity of hydrochloric acid was added and benzene distilled off with steam.

The reaction product was a reddish mass which solidified on cooling and was easily pulverized. It was a mixture of anthrone-benzylidene-acetophenone and two tautomeric substances which will be described below.

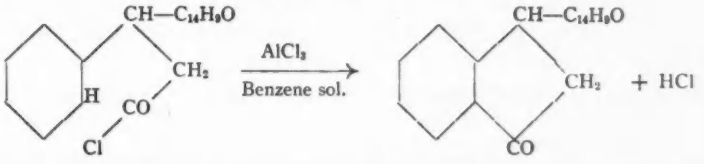
In order to separate anthrone-benzylidene-acetophenone, the raw product was dissolved in the least possible quantity of boiling glacial acetic acid. By cooling, about 8 gm. of a mixture of the two tautomeric substances separated out. They were filtered off and the filtrate containing anthrone-benzylidene-acetophenone was evaporated to dryness. The residue was dissolved in ether and the ethereal solution washed with concentrated ammonia (violet color) and with water. The anthrone-benzylidene-acetophenone remaining behind was recrystallized. It had a light pink color. After recrystallization from alcohol it was colorless; m.p. 115-116° C. Analysis:—Calcd. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47%. Found: C, 86.61, 86.60; H, 5.51, 5.53%.

Part III

γ-ANTHRONYL-α-HYDRINDONE AND ITS DERIVATIVES

In this section will be discussed:—*(a)* the methods by which γ-anthronyl-α-hydrindone was prepared and isolated in two tautomeric forms; *(b)* some derivatives of this ketone; and *(c)* the oxidation of γ-anthronyl-α-hydrindone.

I. *γ-Anthronyl-α-hydrindone.* The synthesis of this ketone was effected by the action of anhydrous aluminium chloride on β-anthronyl-β-phenyl-propionyl chloride dissolved in benzene.

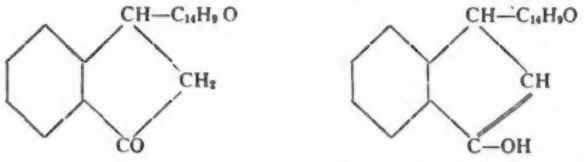


Moreover the benzene reacts with the acid chloride forming fairly large quantities of anthrone-benzylidene-acetophenone. The isolation of this compound was not very difficult, for it is much more soluble in acetic acid than are the other reaction products.

On the other hand, the purification of γ-anthronyl-α-hydrindone is more difficult, for the product separated from anthrone-benzylidene-acetophenone was a mixture of two compounds. It was necessary to recrystallize many times from methyl alcohol to separate them. One crystallizes in diamond-shaped crystals melting at 161-162° C., the other in monoclinic plates melting at 187-188° C.

Theoretically the two compounds obtained could be:—*(a)* two isomeric ketones containing different rings; or *(b)* the enolic form and the ketonic form of the same ketone.

It has been possible to show, as will be seen below, that the two substances are really the two tautomeric varieties of the same ketone:



Preparation.—β-Anthronyl-β-phenyl-propionyl chloride (20 gm.) was dissolved in 200 cc. of anhydrous benzene in a three-necked flask fitted with a mercury seal stirrer and reflux condenser. On the addition of 16 gm. of aluminium chloride, a reddish color appeared. The flask was placed in a water bath at 20° C. and the mixture stirred for three and a half hours. The temperature was then raised till the benzene was boiling, when there was a rapid evolution of hydrochloric acid. After stirring for five hours at that temperature the mixture was cooled and poured on broken ice; a small quantity of hydrochloric acid was added and the benzene was distilled off with steam. The reaction product was a reddish mass which solidified on cooling. This product was a mixture of anthrone-benzylidene-acetophenone and two tautomeric substances which will be described below.

In order to separate anthrone-benzylidene-acetophenone, the raw product was dissolved in the least possible quantity of boiling glacial acetic acid. On cooling, about 8 gm. of a solid mixture melting between 140 and 183° C. separated out. It was filtered off, washed with concentrated ammonia, dried and recrystallized once more from acetic acid. By fractional recrystallization from methyl alcohol two products were obtained:

(A) A colorless solid melting at 161-162° C. and separating from alcohol in diamond-shaped crystals.

(B) A colorless solid melting at 187-188° C. separating in monoclinic crystals.

The results of analyses and the determination of the molecular weights of these two compounds show that they are isomers. Analysis:—*(A)* Calcd. for $C_{28}H_{16}O_2$: C, 85.15; H, 4.96%. Found: C, 85.05, 85.18; H, 5.11, 4.98%. Mol. wt.:—Calcd. 324. Found: 311, 336, 318 (Landsberger). *(B)* Found: C, 85.09; H, 5.08%. Mol. wt. 315, 335.

γ-Anthronyl-α-hydrindone is formed by the method just described, but the yield of pure product is small because the solvent (benzene) reacts to form anthrone-benzylidene-acetophenone.

The yield was increased by the use of carbon disulphide as solvent and the preparation facilitated, for the double aluminium salt formed, which is soluble in benzene, is insoluble in carbon disulphide and could be filtered off. The ketone obtained by the decomposition of the double aluminium salt by water was almost pure and after one crystallization in toluene was composed almost exclusively of the variety melting at 162° C.

β-Anthronyl-β-phenyl-propionyl chloride (57 gm.) was dissolved in 285 cc. of anhydrous carbon disulphide, 59 gm. of aluminium chloride added and the mixture boiled under a reflux condenser for five hours, after which the evolution of hydrochloric acid had practically ceased and the double aluminium salt readily separated. It was filtered off and decomposed with water. Hydrochloric acid was added and steam passed through the mixture for a few minutes. The solid product was filtered off, washed with water, treated with a hot saturated solution of sodium bicarbonate and filtered off again. β-Anthronyl-β-phenyl-propionic acid (6.7 gm.) was obtained by acidifying the filtrate with sulphuric acid.

The dried residue weighed 46.2 gm. and melted at 140-145° C. By recrystallization from toluene, 33.5 gm. was obtained. Yield, 75%; m.p. 159-160° C. After many crystallizations from alcohol the product melted at 161-162° C.

γ-Anthronyl-α-hydrindone is slightly soluble in ether and carbon disulphide, fairly soluble in methyl and ethyl alcohol and very soluble in benzene and toluene. From alcohol and toluene, it separates in diamond-shaped crystals, whereas from carbon disulphide and benzene it separates in needles containing solvent of crystallization. Cold concentrated sulphuric acid dissolves it to form a greenish-yellow solution. The solution was poured into water and the unaltered ketone precipitated. When treated with concentrated alkalies the ketone develops a very intense reddish brown color and partly dissolves. It appears to be more stable towards acids than alkalies.

γ-Anthronyl-α-hydrindone is also formed by dehydration of β-anthronyl-β-phenyl-propionic acid. The temperature at which the experiment must be performed to obtain only one of the two tautomeric forms of the ketone has been determined. β-Anthronyl-β-phenyl-propionic acid (4 gm.) was dissolved in 100 cc. of concentrated sulphuric acid and the solution heated at 103-104° C., when a very sharp change in color was produced. The mixture, up to this point yellow, rapidly became violet colored. This change is probably due to the fact that, besides γ-anthronyl-α-hydrindone, Bz-1-oxy-Bz-3-phenyl-benzanthrone is formed. This compound develops with sulphuric acid a very intense reddish color (5).

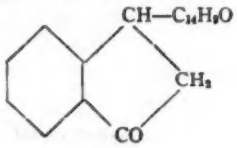
The solution was heated at 110° C. for three minutes and then poured on ice. The ketone precipitated and was filtered off. It was boiled with dilute ammonia (very intense violet color). The ketone, insoluble in ammonia, was filtered off and dried at 100° C.; yield, about 35%. The ketone crystallizes from toluene almost without color and melts at 161-162° C. It was proved identical with γ-anthronyl-α-hydrindone by a mixed melting point determination.

When the raw γ-anthronyl-α-hydrindone obtained by any one of the three methods just described was being purified, it was noticed that the alkaline solution used to purify the ketone developed a very intense violet color, which was particularly intense in the case of the preparation of γ-anthronyl-α-hydrindone with sulphuric acid. It may be due to the presence of traces

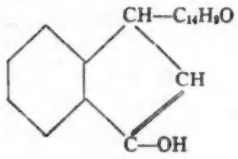
of phenyl-benzanthrone since Bz-1-oxy-Bz-3-phenyl-1-9-benzanthrone treated with alkalies becomes violet colored (5). This has not been proved.

II. *γ-Anthronyl-α-hydrindone Derivatives*

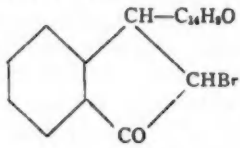
1. ***γ-Anthronyl-β-brom-α-hydrindone.*** As previously stated, when β-anthronyl-β-phenyl-propionyl chloride is treated with aluminium chloride two different compounds are formed, one melting at 162° C., the other at 188° C. The writers ascribe to them the formulas IV and V.



IV



V.



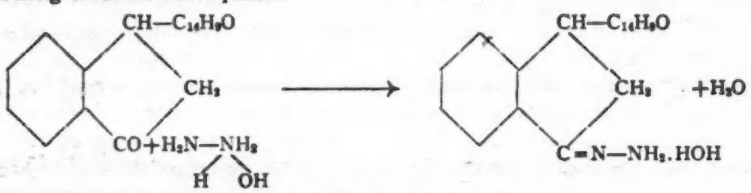
VI.

The writers believe that the two products are tautomers since each gives rise to the same monobromide VI.

Preparation of the monobromide from the product melting at 162° C.—Six grams of the compound melting at 162° C. and 350-400 cc. of ether were treated with bromine (2.8 gm.) and the mixture boiled. After a few minutes, the solution was clear and rapidly became colorless, when crystals of the monobromide were deposited on the wall of the flask. The contents was kept boiling for five hours. After cooling, the crystalline product was filtered off, washed many times with ether and dried in the air. Yield, 6.4 gm.; m.p. 166-167° C. Recrystallized from alcohol, the compound melts at 169-171° C. It is colorless and easily soluble in benzene and toluene; and slightly soluble in carbon disulphide and ether. It separates from alcohol in prisms. Analysis:—Calcd. for $C_{23}H_{15}O_2Br$: Br, 19.82%. Found: Br, 19.60%.

The monobromide from the compound melting at 188°C.—This monobromide was prepared in a manner similar to the one just described. The yield of bromide from 3 gm. of material was 3.2 gm.; m.p. 169-171° C. It is slightly soluble in hot carbon disulphide and hot ether. It is very soluble in hot ethyl or methyl alcohol. Analysis:—Calcd. for $C_{23}H_{15}O_2Br$: Br, 19.82%. Found: Br, 19.78%. Both bromides were proved identical by a mixed melting point determination.

2. ***γ-Anthronyl-α-hydrindone hydrazone.***—The hydrazone was prepared by heating an alcoholic solution of the ketone with hydrazine hydrate. The following reaction takes place:



A hydrate of the hydrazone is obtained.

Twenty grams of the ketone melting at 162° C. was dissolved in the minimum quantity of hot alcohol. Hydrazine hydrate (7.1 gm., 42% in water) was added and the mixture boiled for five hours. The hydrazone, less soluble than the ketone, separated on the walls of the flask. The contents of the flask was cooled at 0° C., the hydrazone filtered off and pressed on a porous porcelain plate. Yield, 17.9 gm. (81.7%).

The hydrazone crystallizes from alcohol in colorless prisms melting with decomposition at 176° C. Analysis:—Calcd. for $C_{23}H_{18}ON_2.H_2O$: N, 7.87%. Found, 7.85%.

3. *γ-Anthronyl-α-hydrindone phenylhydrazone.*—Three grams of the ketone was dissolved in 25-30 cc. of glacial acetic acid, the solution cooled to room temperature and treated with 3 cc. of phenylhydrazine. After standing for ten hours the phenylhydrazone was deposited. It was filtered off and washed many times with alcohol and ether. Yield, 3.9 gm. It was purified by recrystallization from toluene from which it separated in yellow needles; m.p., 224-225° C. It is soluble in toluene and benzene, slightly soluble in alcohol and ether, and insoluble in petroleum ether. The phenylhydrazone crystallized from toluene contains one molecule of this solvent. Analysis:—Calcd. for $C_{29}H_{22}ON_2.C_6H_5.CH_3$: N, 5.53%. Found: N, 5.42, 5.52%.

4. *γ-Anthronyl-α-hydrindone semicarbazone.*—Of the γ-anthronyl-α-hydrindone derivatives the semicarbazone is most readily obtained.

Four grams of the ketone was dissolved in the minimum quantity of hot 95% alcohol. A mixture of 1.42 gm. of semicarbazide hydrochloride and 1.78 gm. of fused sodium acetate, in aqueous solution, was added to the boiling mixture. The solution was boiled under a reflux condenser for six hours. The slightly soluble semicarbazone precipitated and after cooling was filtered off, washed with water and finally with alcohol and ether. Yield, 3.5 gm. The semicarbazone is slightly soluble in most organic solvents. Recrystallized from alcohol it is obtained pure and melts at 243° C. Analysis:—Calcd. for $C_{24}H_{19}O_2N_3$: N, 11.02%. Found: 10.95%.

5. *γ-Anthronyl-α-hydrindone oxime.*—Five grams of the ketone was dissolved in the minimum quantity of alcohol. A mixture of 2·3 gm. of hydroxylamine hydrochloride and 2·7 gm. of fused sodium acetate, in aqueous solution, was added to the boiling alcoholic solution which was kept boiling for 12 hr. After cooling, the solution was filtered and poured into one litre of water. Sulphuric acid was added and the precipitated oxime filtered off, washed with water, and dried. Yield, 4 gm.; m.p. 178-180° C. The oxime was recrystallized from toluene. It was almost colorless, and melted at 181-184° C. The oxime is very soluble in alcohol and ether, less soluble in benzene and toluene. When crystallized from toluene it retains one molecule of solvent, as shown by the results of the analysis. Analysis:—Calcd. for $C_{23}H_{17}O_2N$: N, 3.24%. Found: N, 3.26, 3.25%.

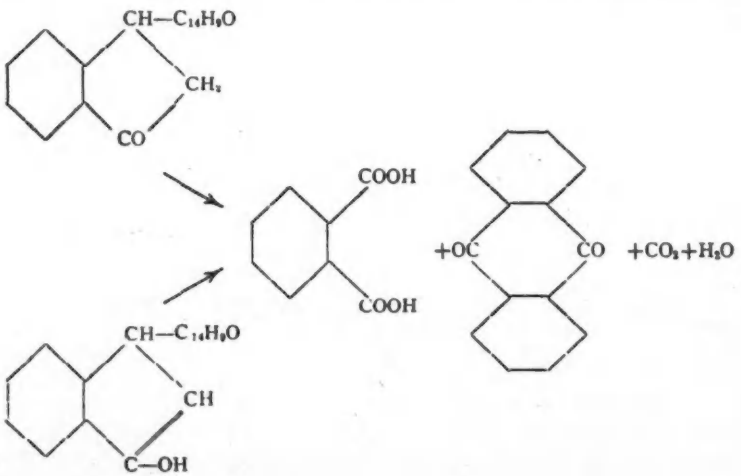
III. *Oxidation Products of γ-Anthronyl-α-hydrindone*

The analyses and the determination of the molecular weights of the two tautomeric forms of the γ-anthronyl-α-hydrindone show that these compounds have the formula $C_{32}H_{16}O_2$. They may then possess the structure of one of the two theoretically possible ketones (I, II) or of their tautomers.

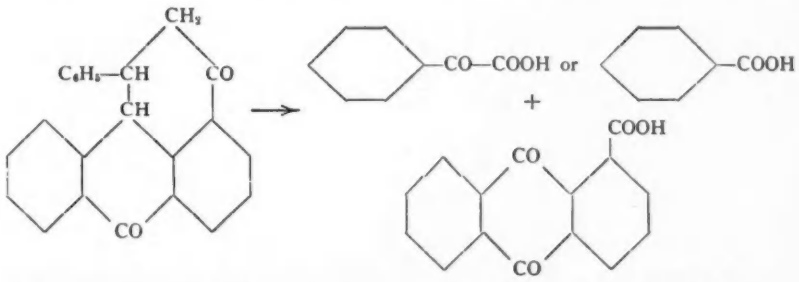
By oxidizing the compounds obtained it has been proved that they are α-hydrindone derivatives. Chromic acid was first used and then nitric acid as oxidizing agent. By using Liebermann and Roka's method (9) and Halley and Marvel's method (3), with chromic acid, anthraquinone was obtained almost exclusively.

On the other hand with nitric acid (sp. gr., 1.2) according to König's method (8) a large quantity of phthalic acid was obtained, besides anthraquinone.

The formation of phthalic acid proves that the tautomers are α-hydrindone derivatives. Oxidation takes place as shown by the following diagram:



The phthalic acid could be formed by oxidation of anthraquinone, but it has been shown that the phthalic acid obtained does not arise from anthraquinone. In fact almost the calculated quantity of anthraquinone and phthalic acid was obtained. This acid then does not come from anthraquinone but from the hydrindone ring. The tautomers produced do not contain the benzanthrone ring; if they did, oxidation would not give rise to anthraquinone but rather to acids, according to the following scheme:



The constitution of the products prepared is then well established.

Oxidation with nitric acid.—The ketone (3.8 gm.) was mixed with 100 cc. of nitric acid (sp. gr., 1.2) and heated to boiling. The ketone was gradually oxidized, a rapid evolution of nitrous vapors taking place. After two hours, the reaction was complete; the mixture was allowed to cool and the yellow insoluble solid filtered off. Dried at 80° C. it weighed 2.4 gm. It was purified by crystallization in acetic acid. There was thus obtained 1.3 gm. of very fine yellow needles melting at 278° C. This product was easily identified as anthraquinone by a mixed melting point determination.

The filtrate was evaporated to dryness on the water bath. About 1.3 gm. of a resinous product remained. It was carefully sublimed and long colorless needles of phthalic anhydride melting at 128° C. were obtained. These crystals were dissolved in boiling water, the aqueous solution filtered and evaporated to dryness. A crystalline colorless product melting at 187° C. was thus obtained. It was identified as phthalic acid by a mixed melting point determination.

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